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MEASUREMENT OF THE COMPLEX SHEAR MODULUS OF A LINEARLY VISCOELASTIC MATERIAL

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Abstract

A detailed description is presented of an experimental system intended to measure the complex shear modulus of homogeneous, isotropic and linearly viscoelastic materials. The test is based on the torsional oscillations of a circular cylindrical sample of finite length. The test and data reduction procedures are described. A Fortran listing of the data reduction computer program is included in the Appendix. Actual measurements are presented on a sample of filled polyvinylchloride. Master curves of the shear storage modulus and shear loss tangent are plotted by making use of the time-temperature shifting principle.

Author

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Introduction

The purpose of the present report is to present a detailed description of an experimental system intended to measure the complex shear modulus of homogeneous, isotropic and linearly viscoelastic materials. We need not be concerned here with the reasons for measuring this particular quantity rather than some other property. This and other such fundamental questions have been discussed at length elsewhere. Suffice to say that a homogeneous, isotropic and linearly viscoelastic material can be partially characterized by the complex shear modulus and this, alone, makes its measurement desirable. The question of completely characterizing the materials of interest is a much more difficult problem and remains a subject of active interest. Furthermore it is not our purpose herein to summarize the many methods proposed for measurement of the dynamic mechanical properties of linearly viscoelastic materials. Instead, reference is made to the following excellent surveys: Ferry, Sawyer and Ashworth (1), Nolle (2), Marvin (3), Abolafia (4) and Ferry (5). In the following we shall try to point out the reasons that still another method is required in addition to those already proposed.

In any experiment the entire system may be regarded as consisting of three sub-systems:

i. the input system which provides and applies the stimulus to the object under test (the power and control system);

ii. the object to be tested (the specimen) and the structure or container intended to hold or contain the specimen in an appropriate attitude (the apparatus); and,

iii. the output system which provides the means for measuring and monitoring the response of the specimen to the applied stimulus (the data acquisition system).

Of these three sub-systems it should be obvious that the second is the most important since it embodies the fundamental idea or concept of the experimental task. It is here that basic creativity enters the experimental system. The success or failure of the entire experimental system depends upon the fundamental idea relating to the manner of accomplishing the experimental task. No matter how elaborate, expensive and accurate the input and output sub-systems may be, the entire experiment is doomed to failure unless the fundamental concept is sound.

Stated in very general terms, every experiment intended to measure material properties consists in two distinct parts. We must have avialable both experimental and analytical solutions of the response of the specimen under the pre-selected stimulus. The analytical solution is formulated in terms of undetermined constants or functions of known variables, referred to as material properties, which are to be determined by comparison with the experimental solution; i.e., the undetermined material properties are evaluated such that the analytical and experimental solutions agree accurately in a numerical sense. We see, therefore, that errors in the measurement of material properties will result not only from inaccuracies in the power and control and data acquisition systems but also from inadequacies in the analytical description of the stress and/or displacement fields in the specimen. It is obvious that all such errors and inaccuracies will be reflected as uncertainties in the values of the material properties. Thus, a candidate test must be such that both experimental and analytical solutions can be performed with the greatest possible accuracy.

Since we are herein concerned with the measurement of the complex shear modulus of homogeneous, isotropic and linearly viscoelastic materials, we must devise a test on a specimen for which the geometry, boundary conditions and stress and displacement fields are not only realizable in the laboratory but are also subject to exact analysis within the framework of the linear theory of viscoelasticity.

An additional desirable quality of a candidate test should be mentioned. In order to completely characterize a linearly viscoelastic material two material property functions are required. It is obvious that two experiments are required, as a minimum, to measure these properties. These experiments may both involve the two properties; one may involve both and the other only a single property function; or both may involve only a single property. Clearly, the latter possibility is the most desirable.

Many of the candidate experiments previously suggested have suffered due to the lack of a specimen with geometry simple enough as to be amenable to both exact analysis and accurate experimental measurement. Exact analysis is more easily accomplished on a specimen in which one dimension is either very large or very small relative to the other dimensions. For example, a very thin plate can be accurately analyzed through the use of a plane stress assumption or the theory of plates depending upon the nature of the stimulus. Similarly, a very long cylinder problem can be accurately solved through the assumption of plane strain. However, successful modeling of these very long or very thin specimens in the laboratory is very difficult. Thus, a specimen is desirable in which all dimensions are finite. Berry (6) has presented the exact solution (within the framework of linear viscoelasticity) for the steady-state, forced, torsional oscillations of a right-circular cylinder of finite length with no limitations on the length-to diameter ratio. In his solution one end of the cylinder is fixed while the other end oscillates sinusoidally in its own plane about the center of symmetry with a known, small angular amplitude and a known frequency. The amplitude of the applied moment at the free end and of the resultant moment at the fixed end and the phase angle between these moments were calculated. It was suggested that if these quantities could be measured experimentally for a sequence of frequency values, a simple method would be available for determining the complex shear modulus over the frequency range used. This experiment possesses all of the requisites mentioned above including the fact that only the complex shear modulus is involved. However, measurement of the amplitude of the torsional moment turns out to be a very difficult experimental task so that while a very sound analytical solution is available, the experimental problem is very difficult, at best.

Gottenberg and Christensen (7) have described an experiment, similar to that described herein, which is a modification of that suggested by Berry. The specimen is the same as Berry's but it is secured to a torsionally-compliant, elastic member which is, in turn, secured to the relatively rigid frame. Rather than measuring the torsional moment at both ends, the angular acceleration at both ends are measured together with the relative phase angle. Some accuracy is sacrificed in this case because the elastic element is modeled as a single degree of freedom spring-mass system. Thus, in order to obtain an experimentally-feasible test, a compromise was required in that a somewhat more complicated analysis was necessary in which some accuracy was sacrificed. Another version of this experiment has been devised and will be described herein. In the following section the three subsystems will be described in detail; the test and data reduction procedures will be presented together with some typical results. It is our opinion that the test described herein is the most sound yet suggested for the measurement of the complex shear modulus of homogeneous, isotropic and linearly viscoelastic materials.

Description of the Experimental System

The experimental system consists in three main sub-systems as previously explained. The complete experimental system is shown in Figs. 1 and 2. In Fig. 1 the apparatus is shown exposed. It is secured to a concrete seismic mass which is used to isolate the apparatus from extraneous distrubances. At the extreme right is the Data Acquisition Console containing most of the data acquisition instrumentation. To the left of this console is the Power and Control Console containing most of the power and control instrumentation. In general, viscoelastic materials are highly temperature dependent. Therefore, it is essential that specimen temperature be controlled. We have chosen the simplest method for accomplishing this purpose by enclosing the entire apparatus in a temperature conditioning chamber as shown in Fig. 2. At the right of the seismic mass we see a multichannel potentiometer which is used as a read-out device for thermocouples distributed throughout the temperature-conditioning chamber for the purpose of monitoring the temperature distribution. As shown in Fig. 2 the experimental system is in complete readiness for a test. Let us now discuss each sub-system in detail.

The Apparatus

By the apparatus we mean that sub-system which includes the entire structural system that holds the specimen in the appropriate attitude so that the stimulus can be applied by the power and control system. We regard the specimen itself as part of the apparatus. The apparatus consists in two sub-assemblies: the specimen sub-assembly and the frame. The seismic mass is included as a part of the frame.

Figure 3 shows the completely assembled specimen sub-assembly. From the bottom up, the sub-assembly consists of the lower torsional spring, the input bell-crank, the specimen, the output bell-crank and the upper torsional spring. The torsional springs have a cruciform cross-section so that they are relatively stiff for axial, bending or transverse motions but relatively compliant for rotational motions. The lower torsional spring is used only for support and alignment purposes. It plays no other role in the test since the angular acceleration of the input bell-crank is maintained constant. The upper torsional spring provides the elastic resistance against which the specimen can deform. The upper torsional spring and the output bell-crank constitute the spring-mass system located between the specimen and frame. Each bell-crank carries two accelerometers, only one of which is active, for the measurement of angular acceleration. The inactive accelerometer on each bell-crank is used for balancing purposes. The input bell-crank serves the additional purpose of converting the rectilinear motion of two electromagnetic vibrators into the angular oscillations transmitted to the specimen. The vibrators are connected to the input bell-crank through small flexures, visible in Fig. 3, in order to minimize the transverse forces which feed back to the vibrators and in order to improve the wave form of the input signal.

The specimen is a right-curcular cylinder that may be solid or hollow. The hollow specimen is preferable since it is easier to machine and allows for more accurate alignment. The dimensions of the specimen are somewhat flexible. Typical dimensions are 1/2 inch diameter by 1-inch length.

The specimen is carefully secured to end-plates with adhesive. A jig is used to minimize misalignments. The end-plates are then secured to the bell-cranks to which are attached the springs thereby completing the assembly. Each element of the specimen sub-assembly is carefully keyed for accuracy of alignment so that only torsional oscillations are experienced by the specimen.

A thick aluminum slab acts as the base for the frame. Two stainless steel columns (2.5 inches diameter) are keyed into the base and support an aluminum cross-head at their upper ends. The columns are threaded at their upper ends so that, with the aid of four, large hexagon nuts, the cross-head can be supported. These elements are overly large so as to maximize apparatus resonances. The specimen sub-assumbly is secured to the frame between the cross-head and base as shown in Fig. 4. The vertical distance between the cross-head and base can be varied to accomodate specimens of different length by repositioning the hexagon nuts.

The base also supports the two electromagnetic vibrators which provide the tangential oscillations to the input bell-crank. The vibrators are part of the Power and Control Sub-System and will be discussed in the next section.

The Power and Control System

This system includes two wholly-independent sub-systems: the Vibration Control Sub-System and the Temperature Conditioning Sub-System. Schematic diagrams of these sub-systems are shown in Fig. 5.

The Vibration Control Sub-System includes three main items of equipment: an oscillator, a power amplifier and two electromagnetic vibrators. The oscillator is an automatic vibration exciter control and is basically an oscillator, a frequency sweep unit, a vibration meter and an automatic level control. The oscillator is a beat frequency oscillator with a frequency range of 5 to 10,000 cps. When the oscillator is used in conjunction with an accelerometer and a cathode follower, the frequency sweep unit, automatically and continuously, varies the frequency at a pre-determined rate over a given frequency range while the automatic level control maintains a pre-selected acceleration (or velocity or displacement) constant throughout the frequency range. The power amplifier is a 200 watt industrial power amplifier with a flat frequency response of 20 to 20,000 cps. The electromagnetic vibrators are of the permanent magnet type with a force rating of 25 pounds and a usable frequency range of 10 to 4000 cps. The operation of this sub-system is self-evident from the schematic diagram shown in Fig. 5. The specific description of equipment used in this sub-system is shown in the list of equipment in Table 1.

Fundamentally, the temperature conditioning sub-system has three parts: a heating circuit, a cooling or refrigeration unit and the temperature conditioning chamber. The chamber is constructed of wood and is insulated with sheets of styro-foam 2.0 inches thick. This chamber covers the entire apparatus, rests on the seismic mass and has a door on one side for ready access to the apparatus. The chamber may be raised from its operational position for apparatus maintenance and specimen changing although it is possible to do the latter with the chamber in operational position. Two enclosed heaters with a circulating blower are mounted on the top of the chamber. The blower is partially isolated from the chamber by a rubber gasket in order to minimize the transmission of extraneous vibrations. The side of the chamber houses the cooling coils and another blower which is also vibration isolated. The coils are cooled by the circulation of freon coolant from the refrigeration unit. When both blowers are in use, a strong air circulation results in a uniform temperature distribution throughout the chamber for temperatures from 25-deg. F to 150-deg. F. In order to maintain chamber temperature constant to within $\pm$ 1-deg. F. the cooling circuit operates continuously while the heating coils are automatically controlled by means of a thermo-switching circuit. An automatic time-switch is used so that the temperature conditioning chamber and its contents can be brought to a steady-state condition during off-hours. The refrigeration unit is housed separately at the base of the seismic mass and contains the compressor, freon storage tank and the motor for the circulation of the freon coolant. This unit is connected to the cooling coil of the chamber by flexible, insulated hosing. Six thermocouples are distributed throughout the chamber and on the apparatus for constant monitoring of the chamber temperature distribution. A multi-channel potentiometer is used as a temperature readout device. The temperature conditioning sub-system was specially manufactured in the University Machine Shops and, for this reason, its component parts are not listed on the list of test equipment.

Data Acquisition System

The function of the data acquisition system is to measure the accelerations of the input and output bell-cranks and the phase angle between these accelerations together with the frequency of the applied harmonic oscillation. In order to accomplish this purpose piezo-electric crystal accelerometers are mounted on the two bell-cranks using electrically insulated studs. The analog voltages from the accelerometers are impedance matched and amplified, with a gain of ten, using a cathode follower with integrated amplifier. The amplified voltages are then used with the automatic vibration exciter for frequency sweeping with automatic level control. During the frequency sweep the signal from the input accelerometer is used with the vibration exciter as a control voltage. The AC signal from the output accelerometer is rectified using a true root mean square voltmeter and applied to the Y-axis of an X-Y plotter. The X axis of the plotter is set on time base and the frequency is noted at convenient intervals during the frequency sweep. This amplification ratio versus frequency plot is used to establish the general nature of the frequency response. Such information is almost indispensable during actual data acquisition.

During the measuring function the amplitude measuring circuit shown in Fig. 6(a) is used. The two analog voltages from the accelerometers are alternately filtered with the same ultra-low frequency, band pass filter and measured with the same true root mean square vacuum tube voltmeter. Filtering minimizes extraneous harmonics and cable noise effects while using the same filter and voltmeter for the two different signals reduces calibration difficulites. The true RMS voltmeter is used in order to minimize the effect of perturbations of the signal caused by extraneous noise.

In measuring the phase angle between the two accelerometer signals we must be careful to account for any phase shifts that are introduced into the system by the electronic circuitry. We can avoid the difficulties in such an accounting by assuring that the phase shifts are the same in the individual accelerometer read-out circuits. This function is accomplished by the phase compensating circuit shown in Fig. 6(b). The voltage level of an AC signal from the oscillator section of the automatic vibration exciter control is reduced to the same voltage level as the amplified accelerometer signals. This standard signal is divided and passed through the individual legs of the accelerometer read-out circuitry which is ultimately used in data acquisition. The phase angle between the signals in the two legs is measured in a counter. In general, this phase angle will not be zero because of phase shifts introduced by the electronic elements in each leg. Now, one of the variable filters is adjusted so that the phase angle is zero, thus assuring that the phase shifts in the two read-out circuits are identical.

Now, the standard signal from the oscillator is replaced by the actual amplified accelerometer signals as shown in Fig. 6(c). The gain of one or the other of the No. 2 amplifiers is adjusted so that the accelerometer signals have the same amplitude. This is done since the counter is amplitude sensitive. Obviously, this gain adjustment does not change the phase relationship. The time interval between corresponding points on the two sine waves is measured in the counter. Triggering circuitry is proivded for this purpose in the particular counter used. This circuitry uses voltage level for triggering and it is for this reason that the amplitudes of the two signals are equalized. In order to measure the frequency accurately, the same counter is used except that now we trigger at the same voltage level on succeeding sine waves of the same signal.

The measured period together with the measured time interval are used to calculate the phase angle between the accelerometer signals.

The schematic diagrams shown in Figs.6 are introduced to simplify the explanation of the various functions. Switching circuits are used in the system in order to accomplish the various steps in the data acquisition procedure as explained above.

The specific equipment used in the data acquisition system is described in Table I.

Test Procedure

The first step in the test procedure is sample preparation. The apparatus is designed to accept solid or hollow circular cylinders with a relatively large range in diameters and lengths. Clearly, hollow specimens are the more desirable since machining and alignment difficulties are minimized. Specimens are drilled and mounted on a mandrel. The outer circumferential surface is then machined to size in a lathe.

The sample is then bonded with a compatible adhesive to steel holders at each end. The hole in the sample is used for alignment with a concentric circular shoulder machined in the holder. The holders are keyed in the apparatus also for alignment purposes. A jig is used during adhesive curing to ensure accurate centering of the sample to the holders. Curing is completed with the sample mounted in the apparatus in order to minimize pre-loading effects.

Prior to testing, the sample is temperature conditioned for at least five hours after the ambient air adjacent to the sample has reached test temperature. The temperature is maintained constant to within 1-deg. F. throughout the conditioning and testing periods.

Before and after each test, the accelerometers are secured with an accurate torque wrench since they have been found to be sensitive to the value of the torque applied in securing them in position.

The apparatus is calibrated at low frequencies (20 to 50 cps) before and after each test by substitution of a steel cylinder for the test specimen. Additionally, a back-to-back calibration is performed on the two read-out accelerometers throughout the frequency range under investigation. Such a calibration is performed prior to each test also.

As previously mentioned, prior to data collection, a plot of amplification ratio versus frequency is made using the automatic vibration exciter control, AD-DC converter and an X-Y plotter. Such a curve establishes the general nature of the frequency response and is invaluable during actual data acquisition.

Since the complex shear modulus is a linear property of viscoelastic materials and since the present experiment is valid only in the linear range of the material under test, a linearity check is performed on the test sample before beginning a series of tests. The linearity check is of a very simple nature in which the input acceleration amplitude is varied. The ratio of the output to the input acceleration - the amplification ratio - is unaffected by such variations in the linear range. Consequently, the linear regime is readily established to ensure that the actual test is performed only in this regime.

The most accurate range for data acquisition is in the neighborhood of the resonant frequency of the coupled sample-output bell-crank-upper torsional spring system. The output bell-crank and upper torsional spring can both be changed at will to provide accurate measurements over as large a frequency range as possible.

Finally, after making all the foregoing tests and checks, the experiment is in a state of readiness for actual data acquisition which is performed by means of the data acquisition system described in the previous section. No further explanation of this procedure seems necessary since this system appears to be reasonably self-explanatory. Now, with the experimental data available, processing of the data is required in order to arrive at the complex shear modulus of the sample under test. We consider this procedure in the next section.

Data Reduction Procedure

In the Introduction to this report, the methodology of materials property testing was discussed. It was pointed out that each such test consists in two distinct parts: analytical and experimental solutions for the response of the specimen under the pre-selected stimulus. Figure 7 shows a schematic drawing of the sample-output bell-crank-upper torsional spring system of the apparatus. In the preceding sections we have described in detail a method for experimentally determining the response of the sample; i.e., the amplification ratio of the output to input accelerations, the phase angle between these accelerations and the corresponding frequency, to a sinusoidally-varying acceleration applied at the lower end ($z = 0$) of the sample. We must now be concerned with developing the analytical solution for this problem together with a data reduction scheme. The latter is simply a method of evaluating the material properties such that both analytical and experimental solutions agree.

An analytical solution for a problem of this general nature has been presented by Berry (6). The reader is thereto referred for a presentation of the general theory. As a mathematical model of the system of Fig. 7 we take a thick-walled cylinder for the sample, ideally-bonded at $z = h$ to a single-degree of freedom torsional spring-mass system, the output bell crank (including appurtenances thereto) being the oscillatory mass and the upper torsional spring being the spring. To be sure, this system is a continuous system with an infinite number of degrees-of-freedom but due to its nature, the fundamental resonant frequency will be very much lower than the next higher resonant frequency. Consequently, within the frequency range of interest, the output bell crank-upper torsional spring system will act much like a single-degree-of-freedom system. We presume the sample is homogeneous and isotropic and we consider it to be purely elastic for the time being. Furthermore, we consider only infinitesimal displacements arriving, thereby, at a linear theory. As a consequence of the manner of application of the stimulus, the symmetry of the system and the manner of support, it seems intuitively clear that the only non-zero component of displacement in the sample is the circumferential displacement u_θ. Furthermore, the only differential equation of motion that is not identically satisfied is given by

$$\frac{\partial^2 u_\theta}{\partial r^2} + \frac{1}{r}\frac{\partial u_\theta}{\partial r} + \frac{\partial^2 u_\theta}{\partial z^2} - \frac{u_\theta}{r^2} = \frac{\rho}{G}\frac{\partial^2 u_\theta}{\partial t^2} \tag{1}$$

wherein we have made use of a system of polar, cylindrical coordinates with the z-axis coinciding with the axis of symmetry of the sample, with the positive direction of the z-coordinates as shown in Fig. 7 and with the origin in the lower face of the sample. The boundary conditions in this problem are given by

$$\ddot{u}_\theta\Big|_{z=0} \equiv \frac{\partial^2 u_\theta}{\partial t^2}\Big|_{z=0} = r\alpha_0 e^{i\omega t} \tag{2a}$$

$$\ddot{u}_\theta\Big|_{z=h} = r\alpha_h e^{i\omega t} \tag{2b}$$

$$T\Big|_{z=h} = J\frac{\ddot{u}_\theta}{r}\Big|_{z=h} + \frac{k u_\theta}{r}\Big|_{z=h} \tag{2c}$$

The first two of these conditions simply express the equality of linear and angular accelerations at the cross-section $z = 0$ and $z = h$, respectively. The latter condition expresses a torque balance at the interface between the sample and the output bell crank.

The problem defined by Eqs. (1) and (2) is essentially equivalent to one solved by Gottenberg and Christensen (7). In the problem solved by these authors the boundary conditions are presented in a slightly different manner but, since the excitation and response of the sample are sinusoidal, their problem is equivalent to that defined by Eqs. (1) and (2). Gottenberg and Christensen solved the elastic problem and then invoked the elastic-viscoelastic correspondence principle to obtain the following solution for the frequency response of the linearly viscoelastic sample:

$$Ae^{-i\phi} = C_1 \Omega^* \sin \Omega^* + \cos \Omega^* \tag{3a}$$

wherein A denotes the ratio of the input to the output accelerations, ϕ is the phase angle between these accelerations and

$$C_1 = \frac{-2(J\omega^2 - k)}{\pi\rho\,\omega^2 h(b^4 - a^4)} \tag{3b}$$

In reality A constitutes the reciprocal of the amplification factor but we are led to a simpler mathematical treatment of the problem if we make use of this reciprocal rather than the amplification factor itself.

The quantities J, k, a, b, h, ρ are all known, measurable parameters of the system or sample. The reciprocal of the amplification factor A, the phase angle ϕ between the input and output accelerations and the corresponding circular frequency ω are quantities measured by means of the experiment described in some detail in previous sections of this report. The only quantities in Eqs. (3a) remaining undetermined are the shear storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, respectively, of the material under test. By equating real and imaginary parts on both sides of Eq. (3a), we obtain two equations for the determination of these unknown quantities. Unfortunately, these are transcendental equations so that we cannot solve for $G'(\omega)$ and $G''(\omega)$ explicitly. Instead, a numerical cut-and-try procedure is required. Such a data reduction procedure has been devised and a complete presentation thereof is included in the Appendix. This presentation is quite complete and self-explanatory so that little additional discussion is required here. We emphasize that the program begins with initial estimates of the shear storage and loss moduli. The program then calculates A and ϕ corresponding to the given circular frequency making use. of Eqs. (3).

Then, the calculated and experimental values of A and ϕ are compared, If the comparison is within the desired accuracy limits, the calculation is complete. If the comparison is not acceptable, the program alters the values of $G'(\omega)$ and $G''(\omega)$ by means of an iteration procedure until acceptable values of A and ϕ result.

Generally, the experimental data is introduced into the data reduction program in order of increasing frequency. Estimates of $G'(\omega)$ and $G''(\omega)$ at the lowest frequency are introduced to start the program but, thereafter, the resulting values for $G'(\omega)$ and $G''(\omega)$ at a given frequency are used as the initial estimates to start the data reduction procedure at the next higher frequency. This method works extremely well as long as the frequency increments are not too large since, then, the changes in the moduli will be relatively small.

Sample Results

In order to illustrate the nature of the information resulting from the test described in previous sections of this report, we have included herein sample results on a specimen of filled polyvinylchloride.

Figures 8 show raw measurements of the amplitude and phase responses of the sample under test. The raw data are plotted as points and an average curve, shown by the solid lines, is passed through the points. The data used for data reduction was obtained from the average curves shown in Figs. 8.

The reduced data are shown in Fig. 9 wherein are plotted curves of the shear stoarge modulus as a function of frequency at the various temperatures used.

Among all materials that satisfy approximately linear viscoelastic laws at uniform temperature are a group which exhibit approximately a particularly simple property with change of temperature. This is a translational shift - no change in shape - of the shear storage modulus plotted against the logarithm of frequency at different uniform temperatures. This property leads to an equivalence relation between temperature and the $\log_{10}$ of frequency which was originally proposed by Leaderman (8) and which has been called the time-temperature shifting principle. This same postulate was introduced in a slightly different form by Ferry (9) and materials exhibiting such behavior have been termed "thermorheologically simple" by Schwarzl and Staverman (10). The postulate has been confirmed experimentally for a variety of viscoelastic materials.

This principle was first applied to experimental data in an explicit numerical fashion by Tobolsky and his coworkers (11). They also introduced and tabulated the shift function $F(T)$ and modified the shifting principle to account for the proportionality of modulus to absolute temperature. Thus, the analytical statement of the time-temperature shifting principle is given by

$$\frac{1}{T} G'_T(f) = \frac{1}{T_0} G'_{T_0}(\xi) \tag{4a}$$

wherein ξ denotes the 'reduced frequency' given by

$$\xi = f a_T \tag{4b}$$

The shift factor a_T is defined in terms of the shift function F(T) by means of

$$F(T) = \log_{10} a_T \tag{4c}$$

The shift function F(T) at the absolute temperature T is the actual amount of shifting required parallel to the $\log_{10} f$ axis in order to superimpose the data collected at the absolute temperature T upon that collected at a reference absolute temperature T_o. In Eq. (4a) G'_T and G'_{T_o} denote the shear storage moduli at the absolute temperatures T and T_o, respectively.

In order to test whether or not the filled polyvinylchloride sample under investigation belongs to the class of thermorheologically simple materials and in order to extend the frequency range of the measurements, the shifting principle was applied to the shear storage modulus data of Fig. 9. The master curve of Fig. 10(a) is the result, The reference temperature selected was 65 deg. F. and the shift factor a_T required is plotted as a function of temperature in Fig. 11.

Using this same shift factor the master curve for the shear loss tangent was constructed with the result shown in Fig. 10(b). In this case the procedure was somewhat different. The data reduction procedure yeilds the shear loss modulus G" as well as the shear storage modulus G'. Their ratio constitutes the shear loss tangent. As a consequence of experience with this type of experiment, we know that accurate measurement of shear loss tangent is extremely difficult. Therefore, in the data reduction process concerning the loss tangent we have restricted the usable data to the immediate neighborhood of the resonant frequency since this region is the region of greatest accuracy. Thus, in Fig. 10(b) we see six small packets of data points each restricted to the neighborhood of the resonant frequency of the system at the temperature indicated.

From Figs. 10 it seems clear that the filled polyvinylchloride sample is, indeed, thermorheologically simple. Therefore, we have, in effect, extended the frequency range over which the measurements were made. Figs. 10 also reveal the fact that we have not completed the measurement of the shear properties of the sample. The master curve for the storage modulus is by no means complete since it must tend to constant values at both frequency extremes. On the other hand, the master curve for the shear loss tangent is expected to display a maximum and then tend to zero at the extreme frequencies. Since the material is thermo-rheologically simple, the master curves could have been completed by performing measurements at higher and lower temperatures. Unfortunately, our temperature conditioning system does not have an adequate temperature range.

References

1. Ferry, J.D., W.M. Sawyer and J.N. Ashworth, "Behavior of Concentrated Polymer Solutions under Periodic Stresses" J. Polymer Science 2 593 (1947)

2. Nolle, A.W., "Methods for Measuring Dynamic Mechanical Properties of Rubber-Like Materials" J. Appl. Physics 19 753 (August 1948)

3. Marvin, R.S., "Measurement of Dynamic Properties of Rubber" Industrial and Engineering Chemistry 44 696 (April 1952)

4. Abolafia, O.R., "Survey of Methods Used to Determine the Dynamic Mechanical Properties of Polymers" Picatinny Arsenal Tech. Rep. No. 2060 (September 1954)

5. Ferry, J.D., Viscoelastic Properties of Polymers John Wiley and Sons, Inc. New York (1961)

6. Berry, D.S., "Stress Propagation in Visco-Elastic Bodies" J. Mech. and Physics of Solids 6 177 (1958)

7. Gottenberg, W.G., and R.M. Christensen "On the Determination of the Complex Shear Modulus of a Linear, Isotropic Viscoelastic Solid" Space Technology Laboratories, Inc., Redondo Beach, Calif., Tech. Report No. 6121-6777-RUOOO/EM 13-14 (1 June 1963)

8. Leaderman, H., "Elastic and Creep Properties of Filamentous Materials" Textile Foundation, Washington, D.C. (1943), p. 175

9. Ferry, J.D., "Mechanical Properties of Substances of High Molecular Weight VI. Dispersion in Concentrated Polymer Solutions and its Dependence on Temperature and Concentration" J. Amer. Chem. Soc. 72 3746 (1950)

10. Schwarzl, F., and A.J. Staverman "Time-Temperature Dependence of Linear Viscoelastic Behavior" J. Appl. Phys. 23 838 (1952)

11. Tobolsky, A.V., and J.R. McLoughlin "Elastoviscous Properties of Polyisobutylene V. The Transition Region" J. Polymer Science 8 543 (1952)

Notation

r, θ, z	coordinate variables of a system of polar, cylindrical coordinates
t	time
u_θ	circumferential component of displacement
ρ	mass density of the material of the sample
G	elastic shear modulus
$G^*(i\omega)$	complex shear modulus = $G'(\omega) + i\,G''(\omega)$
$G'(\omega)$	shear storage modulus
$G''(\omega)$	shear loss modulus
ω	circular frequency
f	frequency in cycles per second
α_o	angular acceleration at $z = 0$
α_h	angular acceleration at $z = h$
T	internal torsional moment; absolute temperature in degs. Rankine
J	polar moment of inertia of output bell crank including appurtenances thereto
k	spring modulus of upper torsional spring (torque per unit of angular displacement)
A	reciprocal of the amplification factor = α_o/α_h
ϕ	phase angle between the input and output accelerations
Ω^*	frequency coefficeint = $\sqrt{\rho\omega^2 h^2 / G^*(i\omega)}$
a	inner radius of sample
b	outer radius of sample
h	sample length
ξ	reduced time = f/a_T

a_T	shift factor at absolute temperature T
F(T)	shift function at absolute temperature T = $\log_{10} a_T$

APPENDIX

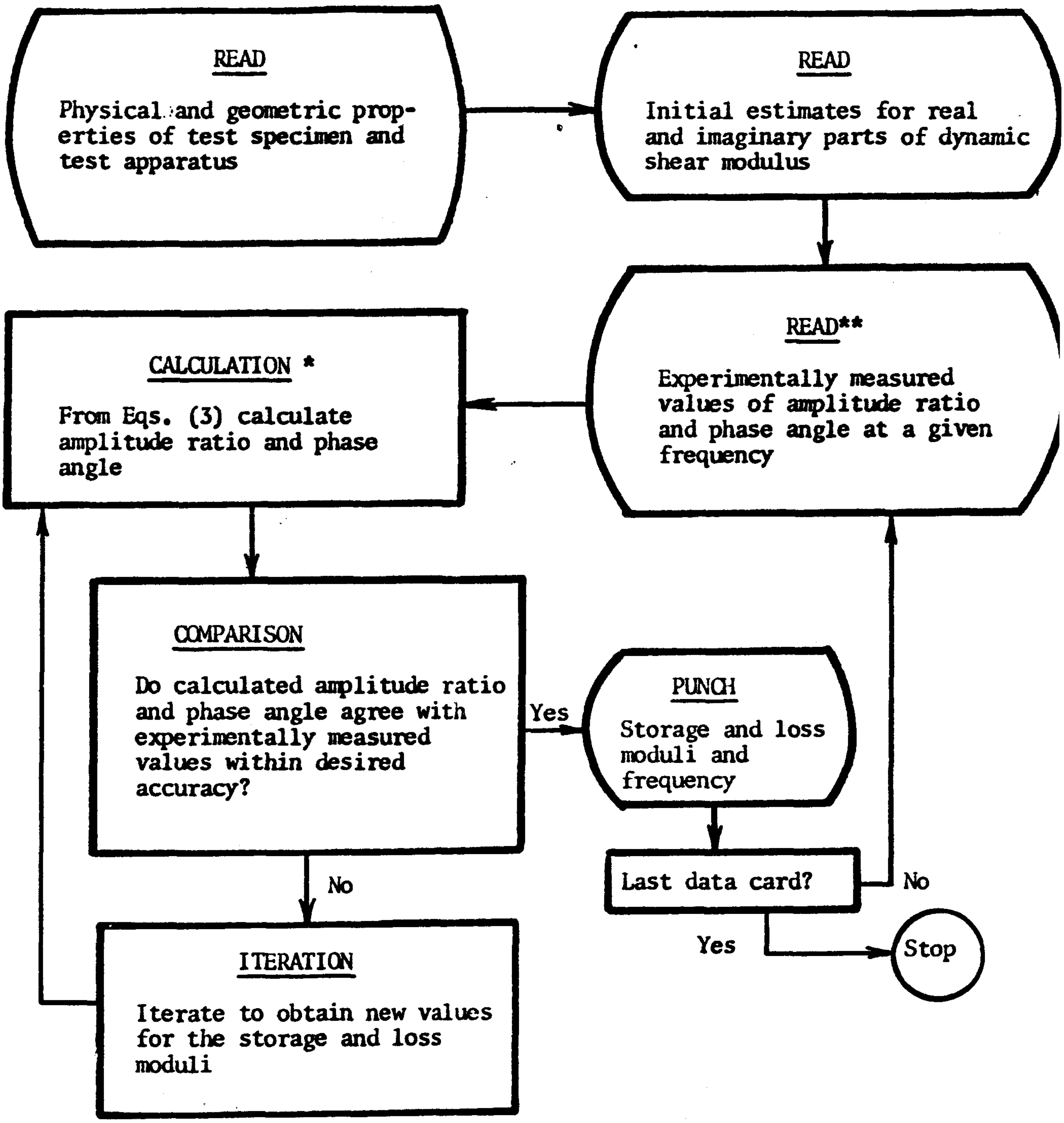
Data Reduction Program

List of Symbols

Mathematical Symbol	Fortran Symbol	Description
a	A	Inner radius of specimen in inches
b	B	Outer radius of specimen in inches
w	RHI	Specific weight of specimen in lbs./cu. in.
J	FJ	Polar moment of inertia of output bell crank system in lb.-in.-(sec.)^2
k	FK	Torsional spring constant of upper torsional spring in in.-lb./radian
Scale	SCALE	Accelerometer calibration factor
δ_1	SD_1	Desired convergence accuracy of G'
δ_2	SD_2	Desired convergence accuracy of G"
Δ_1	DEL1	G' iteration parameter (usually 10 per cent)
Δ_2	DEL2	G" iteration parameter (usually 5 per cent)
KK	KK	Maximum number of iterations desired (usually 20)
-	K	Indicates last card if $K > 0$
G'_{IE}	G1P	Initial estimate for $G'(\omega)$
G''_{IE}	G2P	Initial estimate for $G''(\omega)$
A_{exp}	AMP	Experimentally measured amplitude ratio (output acceleration/input acceleration)
ϕ_{exp}	PHO	Experimentally measured phase angle in degrees
f	FR	Frequency in cps at which A_{exp} and $_{exp}$ were measured
Ω'	O1	Real part of dimensionless frequency coefficient

Ω''	O2	Imaginary part of dimensionless frequency coefficient
ψ	PSI	Angle relating
C_1	C1	Geometrical constant proportional to frequency
A_{Re}	AR	Real part of calculated amplitude ratio
A_{Im}	AI	Imaginary part of calculated amplitude ratio
A_{calc}	F(M)	Calculated amplitude ratio
$\phi calc$	F(M+1)	Calculated phase angle
F_i	F_i	Terms defined in interation routine (i=7,8, ..., 18)
G'	G1	Calculated (iterated) value for G'
G''	G2	Calculated (iterated) value for G''
h	H	Length of specimen in inches

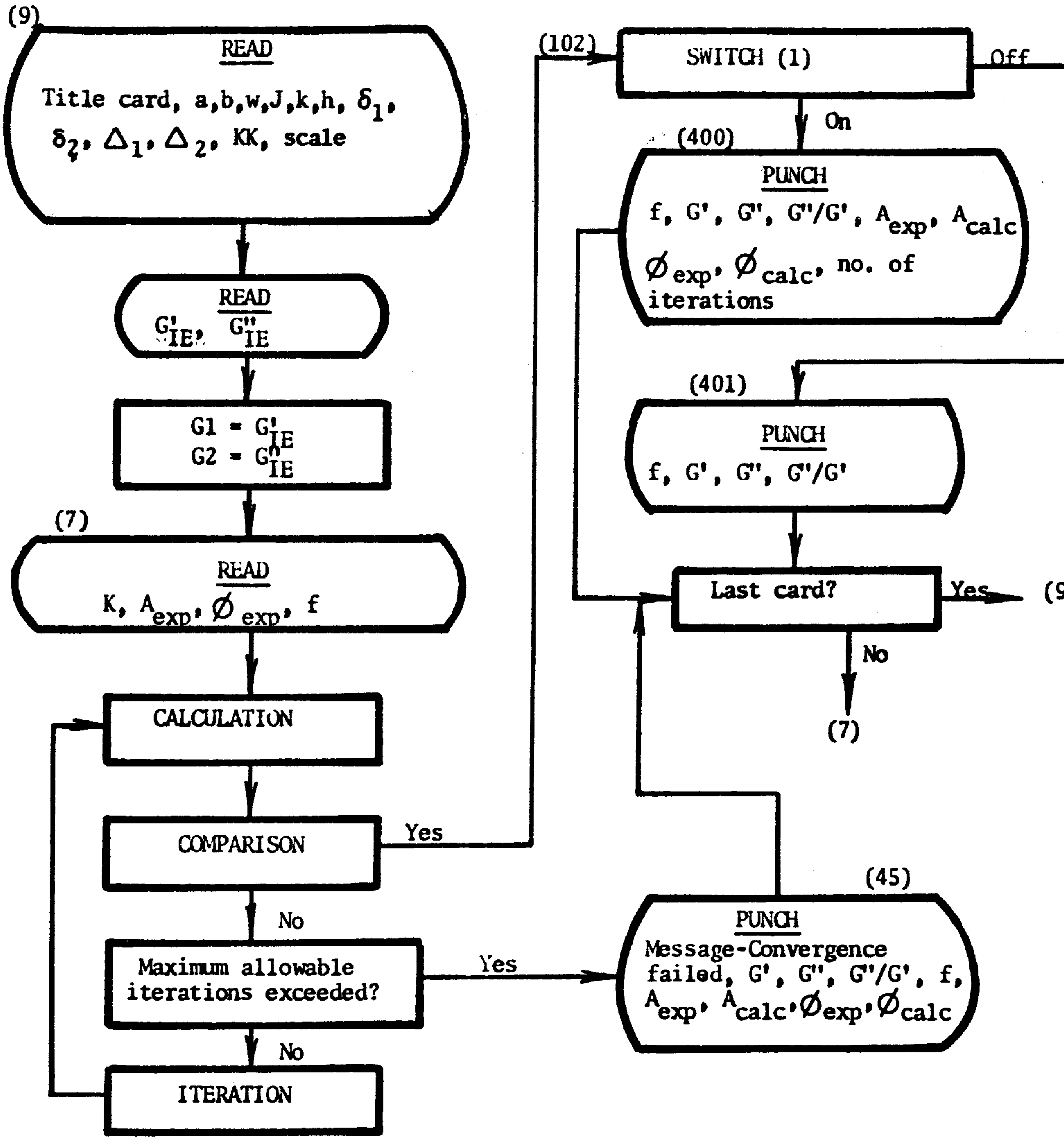
General Flow Chart



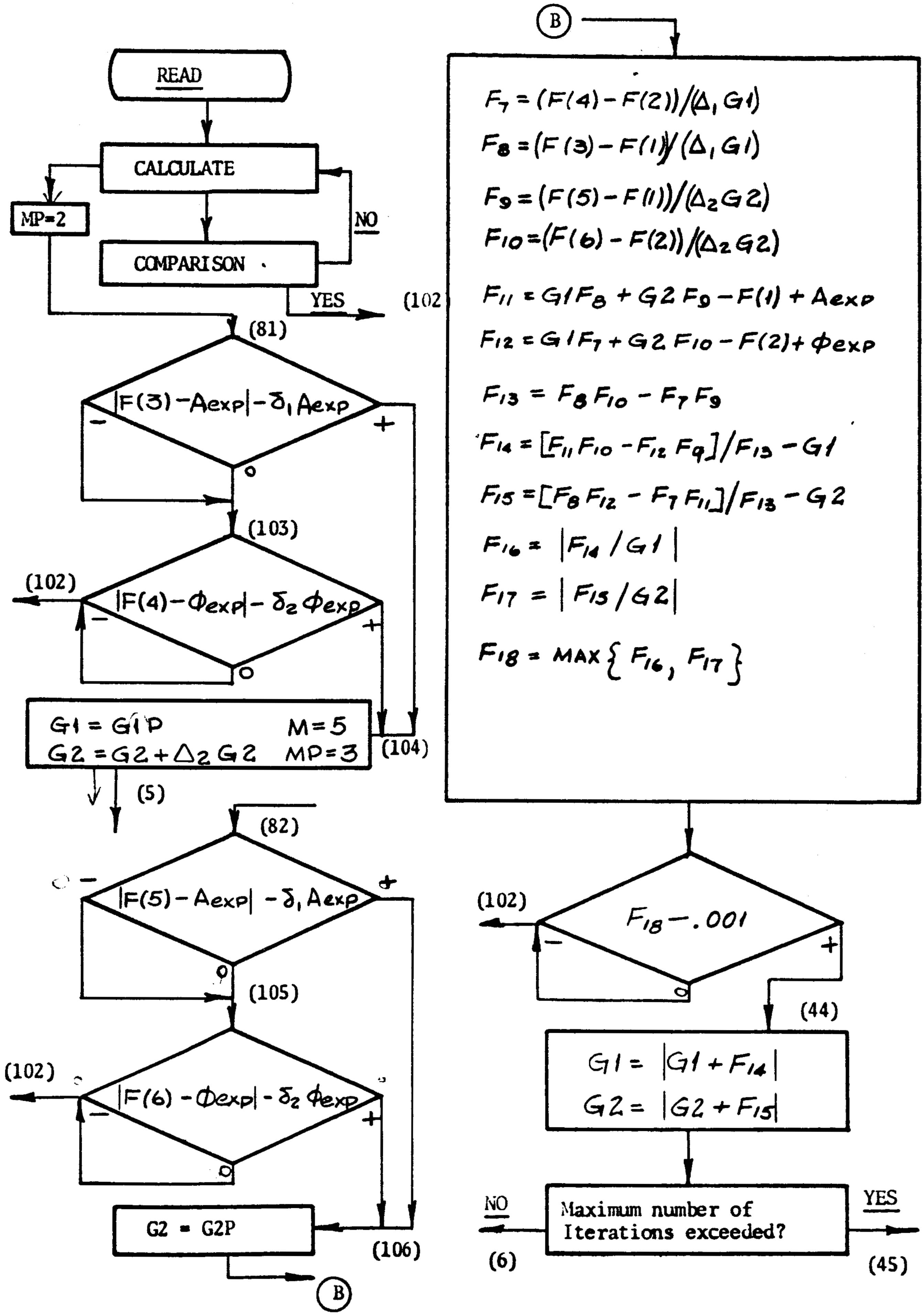
* Eqs. (3) use the initial estimates for G' and G" to initiate the program. Thereafter, the values obtained from the iteration routine are used. For all new data (for the same sample) the previously calculated values of G' and G" are used for the initial estimates.

** Data should be introduced such that each new frequency is greater than the previous one.

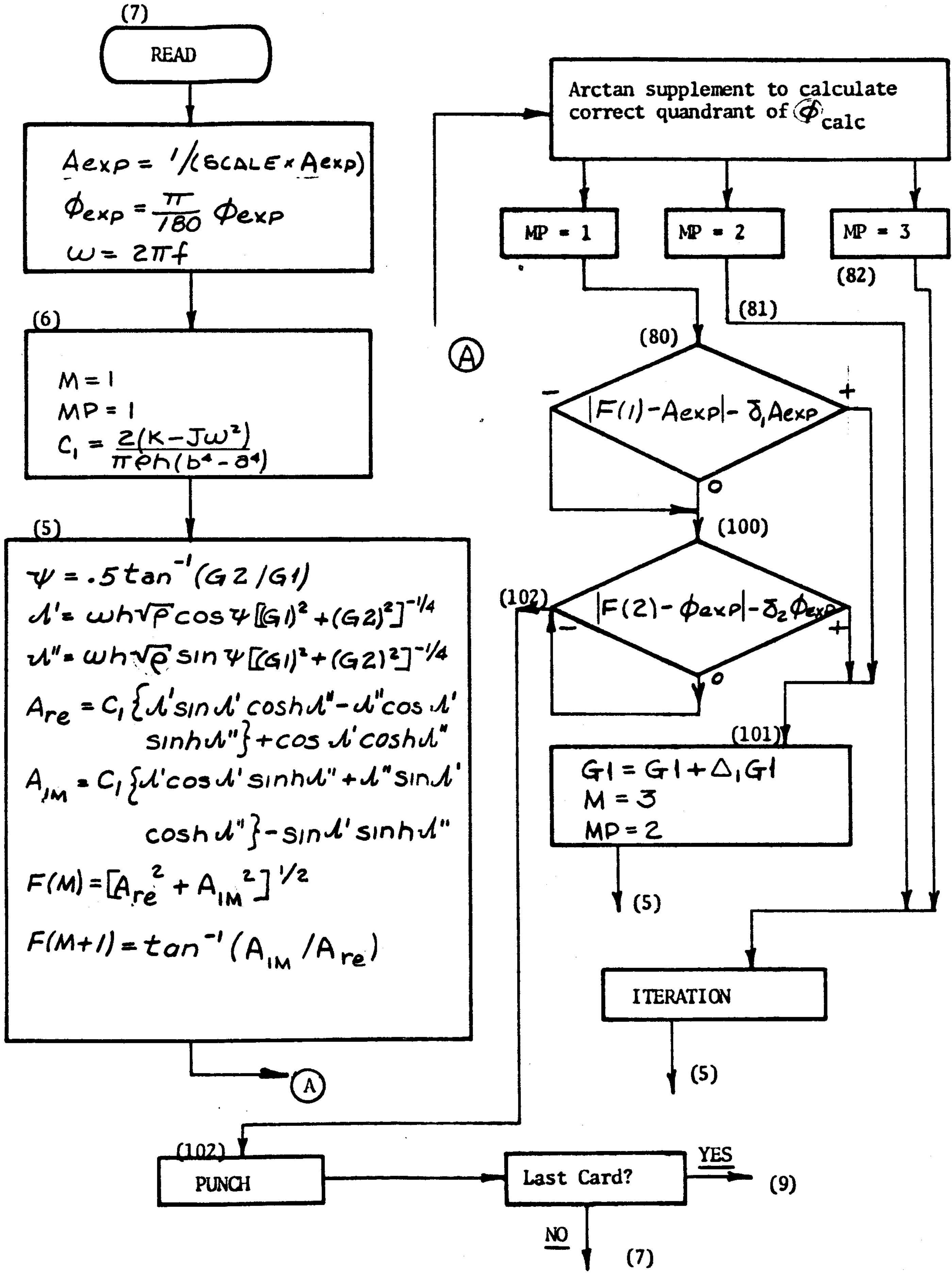
Input-Output Flow Chart



ITERATION FLOW CHART



CALCULATION - COMPARISON FLOW CHART



```
C     MATERIAL PROPERTIES PROGRAM TO OBTAIN  COMPLEX SHEAR
C     MODULUS  FROM HIGH FREQUENCY TORSION DATA
C     INPUT PHASE ANGLE MUST BE NEGATIVE
C     SW 1 OFF FOR COLUMN PRINT OUT
      DIMENSION F(6)
    1 FORMAT(5E14.8)
    2 FORMAT(I2,3E14.8)
    3 FORMAT(49H                                                 )
  300 FORMAT( /24HSPECIMEN CHARACTERISTICS)
  301 FORMAT( 3X13HINNER RADIUS=F7.4,3HIN.4X13HOUTER RADIUS=F7.4,3HIN.)
  302 FORMAT( 3X7HLENGTH=F7.4,3HIN.10X8HDENSITY=F7.4,10HLB./IN.**3)
  303 FORMAT( /23HFIXTURE CHARACTERISTICS)
  304 FORMAT( 3X24HPOLAR MOMENT OF INERTIA=F8.5,1X15HLB.-IN.-SEC.**2)
  305 FORMAT( 3X16HSPRING CONSTANT=F9.3,1X7HLB.-IN.)
  306 FORMAT( /8HACCURACY)
  309 FORMAT( 3X15HCONV. TO WITHINF5.2,1X19HPCT. OF GIVEN AMPL.)
  310 FORMAT( 3X15HCONV. TO WITHINF5.2,1X19HPCT. OF GIVEN PHASE)
  311 FORMAT( /27HACCELEROMETER SCALE FACTOR=F7.4)
  320 FORMAT(//6HFREQ.=F8.2,1X3HCPS11X19HGIVEN AMPL.(CORR.)=F7.4)
  321 FORMAT(3X9HRE(G*)=  F10.2,7X12HCALC. AMPL.=F7.4)
  322 FORMAT(3X9HIMAG(G*)=F10.2, 7X12HGIVEN PHASE=F8.3)
  323 FORMAT(//31HFOLLOWING CASE DID NOT CONVERGE)
  324 FORMAT(3X10HLOSS TANG=F7.4,9X12HCALC. PHASE=F8.3)
  325 FORMAT( 13HRUN COMPLETED)
  326 FORMAT(20X13HNO. OF ITER.=I2)
  404 FORMAT(F8.2 ,2F13.2,F10.4)
  408 FORMAT(//2X5HFREQ.7X6HRE(G*)6X8HIMAG(G*)4X4HLOSS)
  409 FORMAT(2X5H(CPS)7X5H(PSI) 8X5H(PSI)5X7HTANGENT)
  410 FORMAT(4X15HZERO DIVISOR ATF6.0,1X3HCPS)
    9 READ 3
      READ 1,A,B,H,RHI
      READ 2,KK,FJ,FK
      READ 1,DEL1,DEL2,SD1,SD2,SCALE
      READ 1,G1P,G2P
      PUNCH 3
      PUNCH 300
      PUNCH 301,A,B
      PUNCH 302,H,RHI
      PUNCH 303
      PUNCH 304,FJ
      PUNCH 305,FK
      PUNCH 311,SCALE
      PUNCH 306
      SD10=SD1*100.
      SD20=SD2*100.
      PUNCH 309,SD10
      PUNCH 310, SD20
      IF(SENSE SWITCH 1)406,407
```

```
  407 PUNCH 408
      PUNCH 409
  406 PI=3.1415926
      RHO=RHI/385.
      D1=PI*RHO*H*(B**4-A**4)
      D2=H*SQRTF(RHO)
   61 G1=G1P
      G2=G2P
    7 N=0
C
C     READ EXP. PHASE AND AMPL. AT A FREQ.
C
      READ 2,K,FR,AMP,PHO
      AMP=1./(AMP*SCALE)
      PHI=PHO*.017453292
      DA=SD1*AMP
      DP=ABSF(SD2*PHI)
      W=2.*PI*FR
      W2=W*W
      D2OW=D2*W
    6 M=1
      MP=1
      C1=2.*(-FJ*W2+FK)/(W2*D1)
      GO1=G1
      GO2=G2
      GO21=GO2/GO1
C
C     CALC. OF AMPL. AND PHASE FROM EQ. 3
C
    5 D3=D2OW/((G2*G2+G1*G1)**.25)
      PSI=.5*ATANF(G2/G1)
      O1=D3*COSF(PSI)
      O2=D3*SINF(PSI)
      EPX=EXPF(O2)
      REPX=1./EPX
      COSH=.5*(EPX+REPX)
      SINH=.5*(EPX-REPX)
      CO=COSF(O1)
      SI=SINF(O1)
      AR=C1*(O1*SI*COSH-O2*CO*SINH)+CO*COSH
      AI=C1*(O1*CO*SINH+O2*SI*COSH)-SI*SINH
      F(M)=SQRTF(AR*AR+AI*AI)
C
C     DET. OF CORRECT QUADRANT FOR CALC. PHASE ANGLE
C
      IF(AR)504,505,504
  504 F(M+1)=ATANF(AI/AR)
      IF(F(M+1))605,700,607
  605 IF(AR)610,610,700
```

```
  610 F(M+1)=PI+F(M+1)
      GO TO 700
  607 IF(AR)615,700,700
  615 F(M+1)= F(M+1)-PI
      GO TO 700
  505 IF(AI)507,508,509
  507 F(M+1)=-PI*.5
      GO TO 700
  508 F(M+1)=0.0
      GO TO 700
  509 F(M+1)=PI*.5
  700 GO TO (80,81,82),MP
C
C     COMPARISON OF CALC. TO EXP.
C
   80 IF(ABSF(F(1)-AMP)-DA)100,100,101
  100 IF(ABSF(F(2)-PHI)-DP)102,102,101
C
C     ITERATION ROUTINE TO FIND NEW SHEAR MOD.
C
  101 G1=G1+DEL1*G1
      M=3
      MP=2
      GO TO 5
   81 IF(ABSF(F(3)-AMP)-DA)103,103,104
  103 IF(ABSF(F(4)-PHI)-DP)102,102,104
  104 G1=G01
      G2=G2+DEL2*G2
      M=5
      MP=3
      GO TO 5
   82 IF(ABSF(F(5)-AMP)-DA)105,105,106
  105 IF(ABSF(F(6)-PHI)-DP)102,102,106
  106 G2=G02
      DS1=DEL1*G1
      DS2=DEL2*G2
      F7=(F(4)-F(2))/DS1
      F8=(F(3)-F(1))/DS1
      F9=(F(5)-F(1))/DS2
      F10=(F(6)-F(2))/DS2
      F11=G1*F8+G2*F9-F(1)+AMP
      F12=G1*F7+G2*F10-F(2)+PHI
      F13=F8*F10-F7*F9
      IF(F13)50,55,50
   55 PUNCH 410,FR
      PRINT 410,FR
      GO TO 61
   50 F14=(F11*F10-F12*F9)/F13-G1
```

```
      F15=(F8*F12-F7*F11)/F13-G2
      F16=ABSF(F14/G1)
      F17=ABSF(F15/G2)
      IF(F16-F17)40,40,41
   40 F18=F17
      GO TO 42
   41 F18=F16
   42 IF(F18-.001)102,102,44
   44 G1=ABSF(G1+F14)
      G2=ABSF(G2+F15)
      N=N+1
      IF(N-KK)6,6,45
C
C     OUTPUT IF CONV. FAILS AFTER KK ATTEMPTS
C
   45 PUNCH 323
      PRINT 323
      DF2=F(2)/.017453292
      AMP=1./AMP
      F(1)=1./F(1)
      PUNCH 320,FR,AMP
      PUNCH 321,G01,F(1)
      PUNCH 322,G02,PHO
      PUNCH 324,G021,DF2
      IF(K)7,7,8
C
C     SW 1 ON GIVES DETAILED PRINTOUT
C     SW 1 OFF GIVES JUST FREQ. AND SHEAR MOD.
C
  102 G21=G2/G1
      IF(SENSE SWITCH 1)400,401
  401 PUNCH 404,FR,G1,G2,G21
      GO TO 402
  400 DF2=F(M+1)/.017453292
      AMP=1./AMP
      F(M)=1./F(M)
      PUNCH 320,FR,AMP
      PUNCH 321,G1,F(M)
      PUNCH 322,G2,PHO
      PUNCH 324,G21,DF2
      PUNCH 326,N
  402 IF(K)7,7,8
    8 PRINT 325
      GO TO 9
      END
```

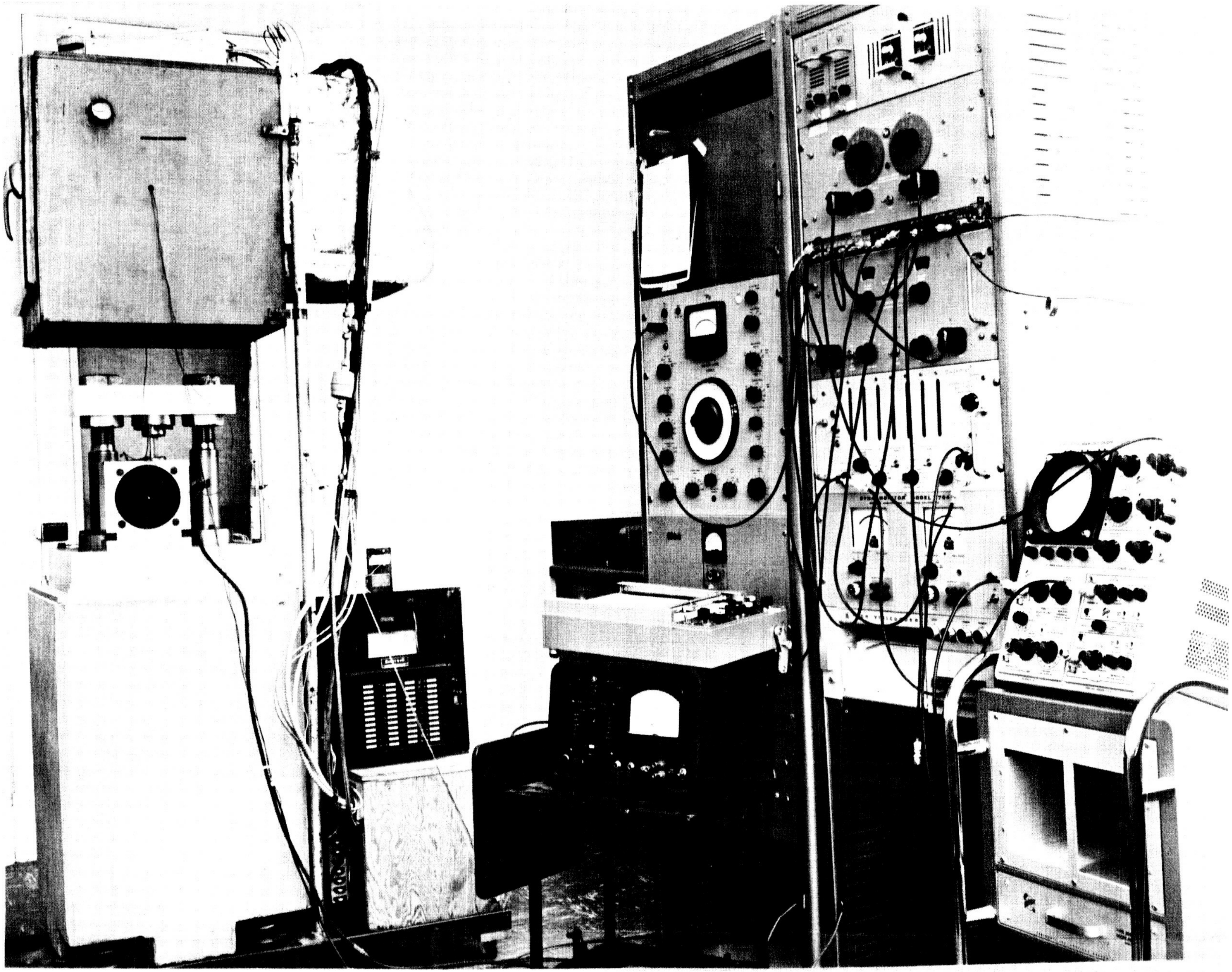


Fig. 1. Long-Range View of Experimental System with Temperature-Conditioning Chamber Raised to Expose Apparatus.

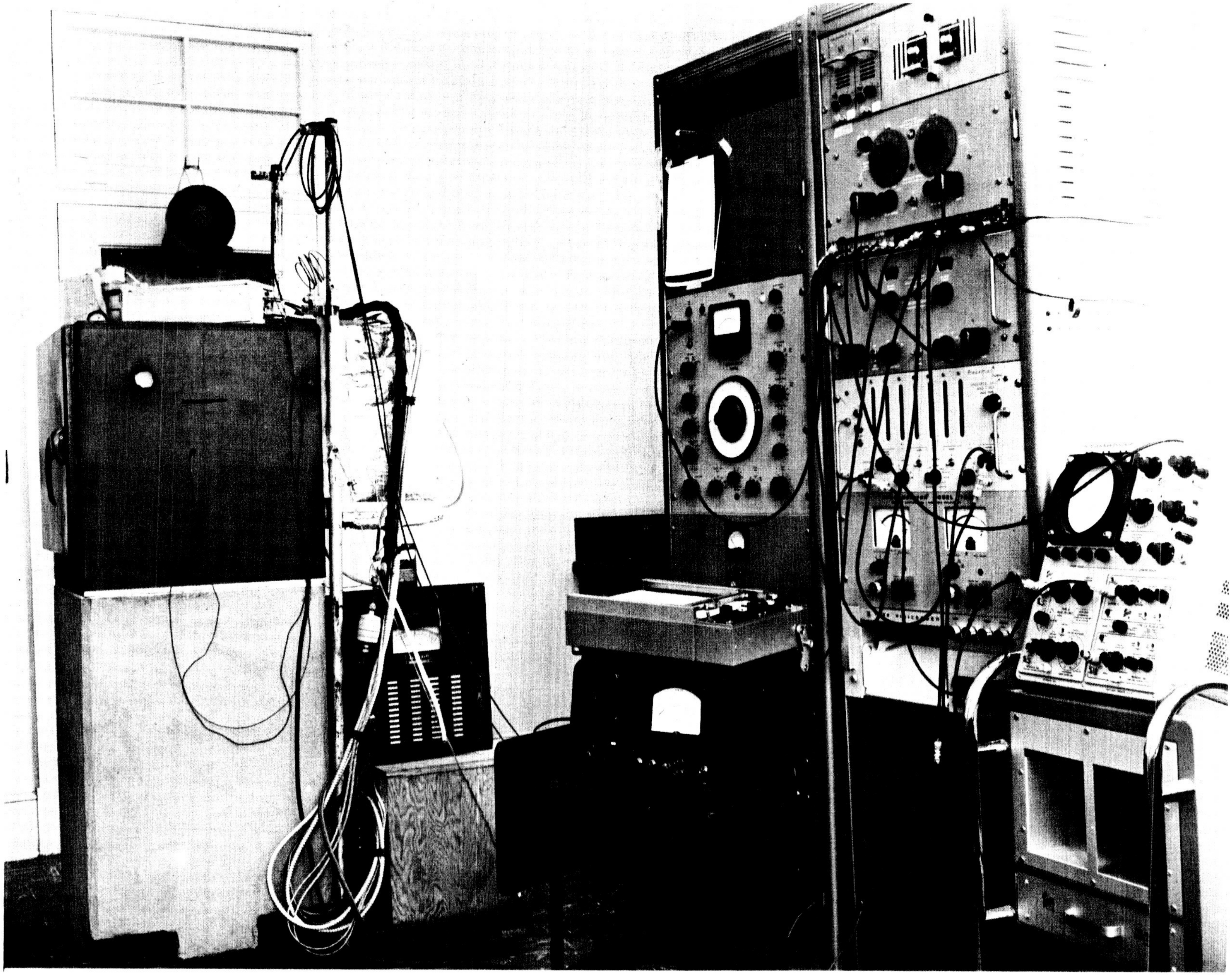


Fig. 2. Long-Range View of Experimental System Ready for Operation.

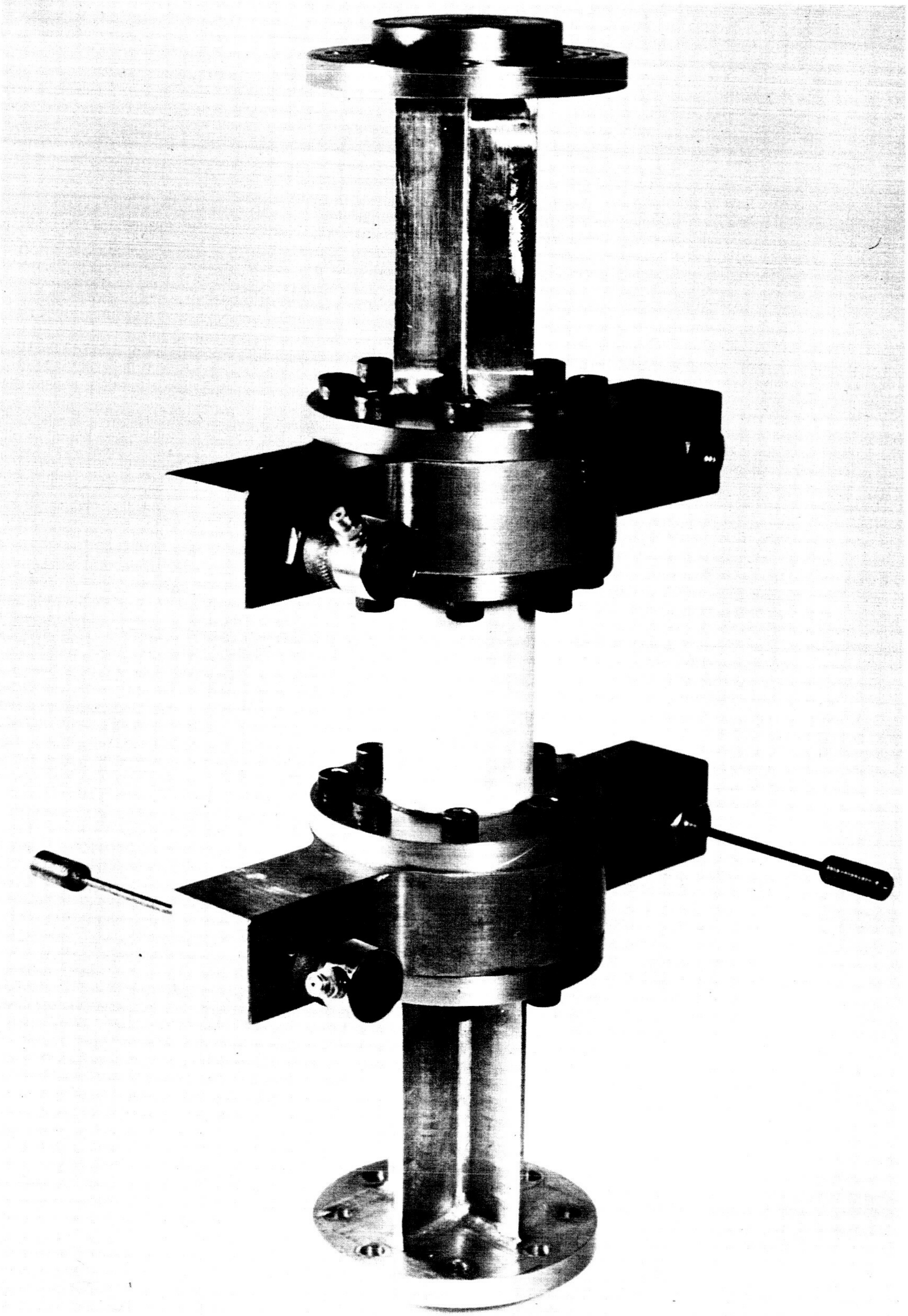


Fig. 3. Apparatus Sub-Assembly Including Upper and Lower Torsional Springs, Upper and Lower Bell-Cranks and Specimen.

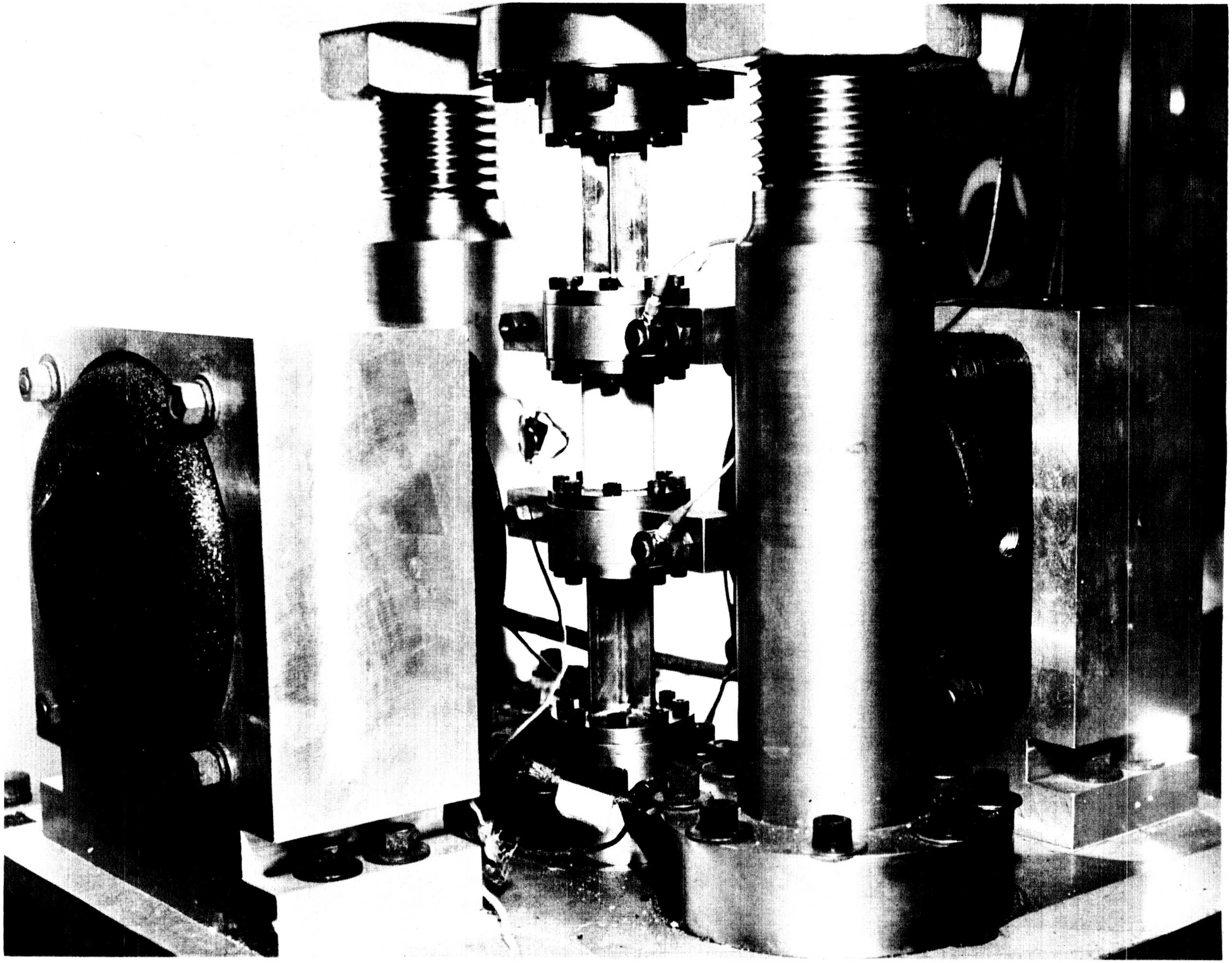
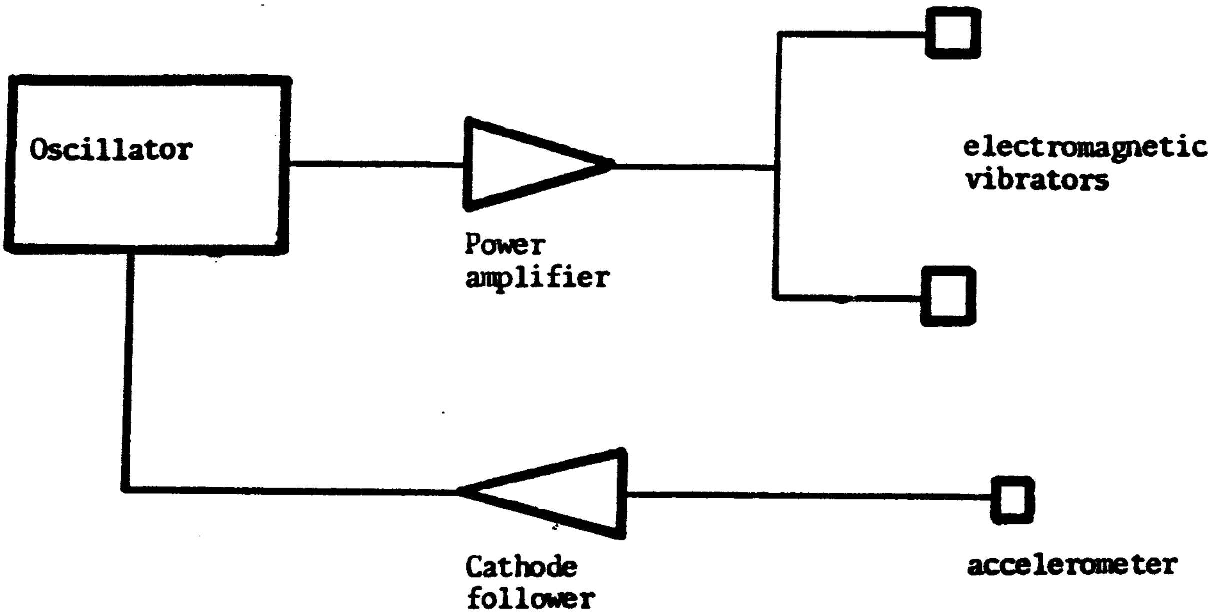
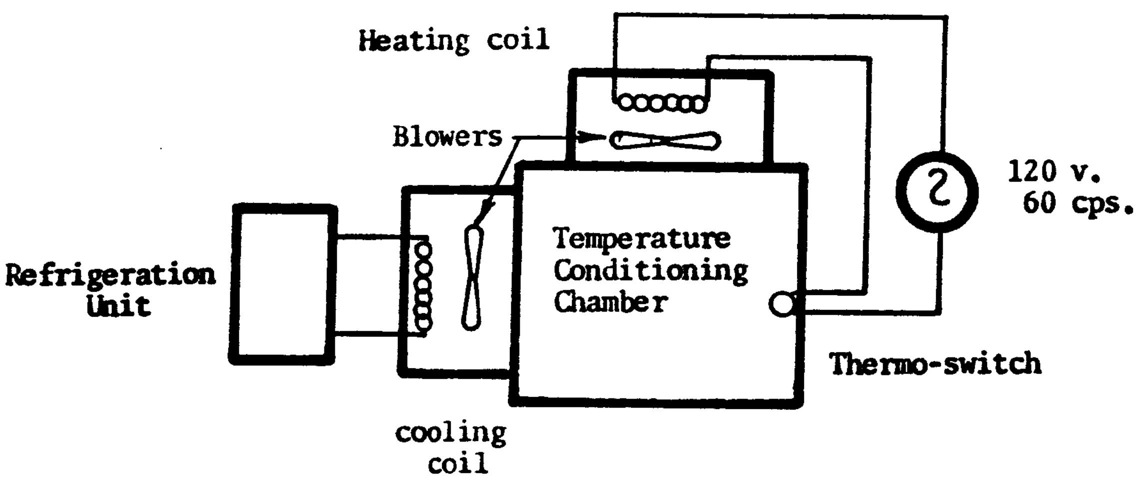


Fig. 4. Close-Up of Apparatus Showing Specimen in Place.

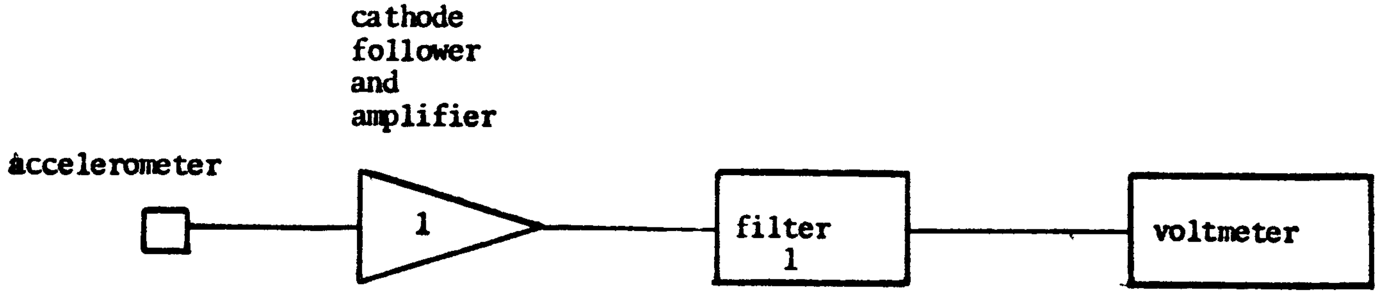


a. Vibration Control Sub-System

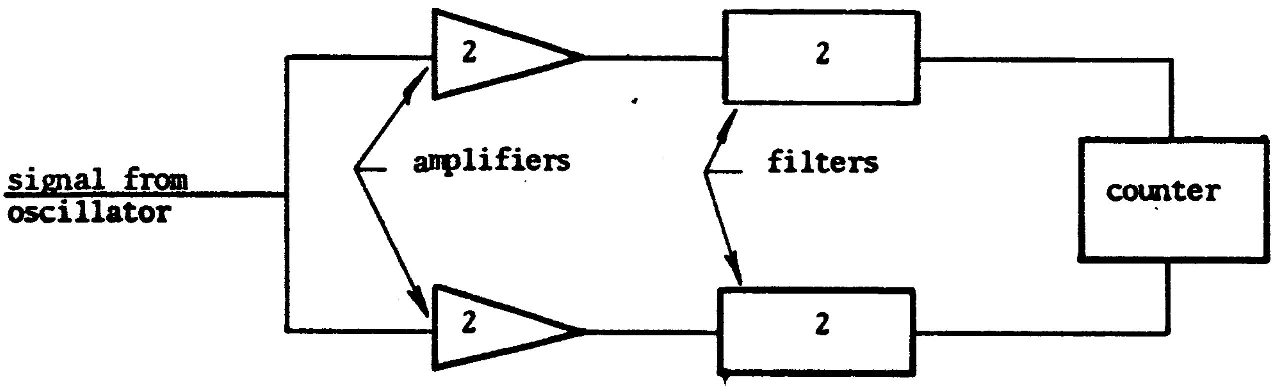


b. Temperature Conditioning Sub-System

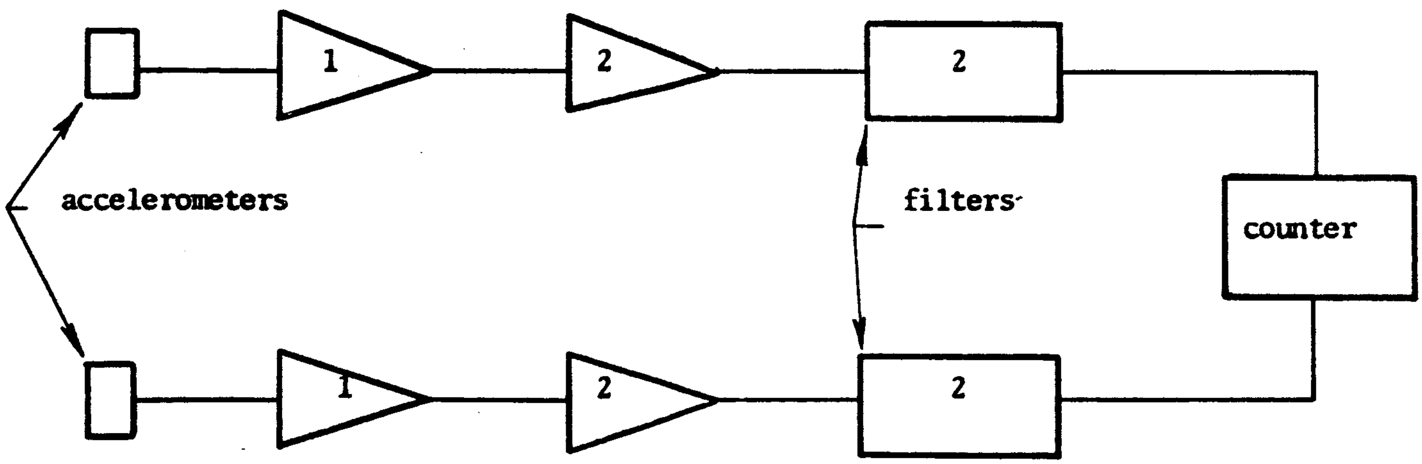
Fig. 5 The Power and Control System



a. Amplitude Measuring Circuit



b. Phase Compensating Circuit



c. Frequency and Phase Measuring Circuit in Operational Mode

Fig. 6 Schematic Diagrams of Various Circuits in the Data Acquisition System

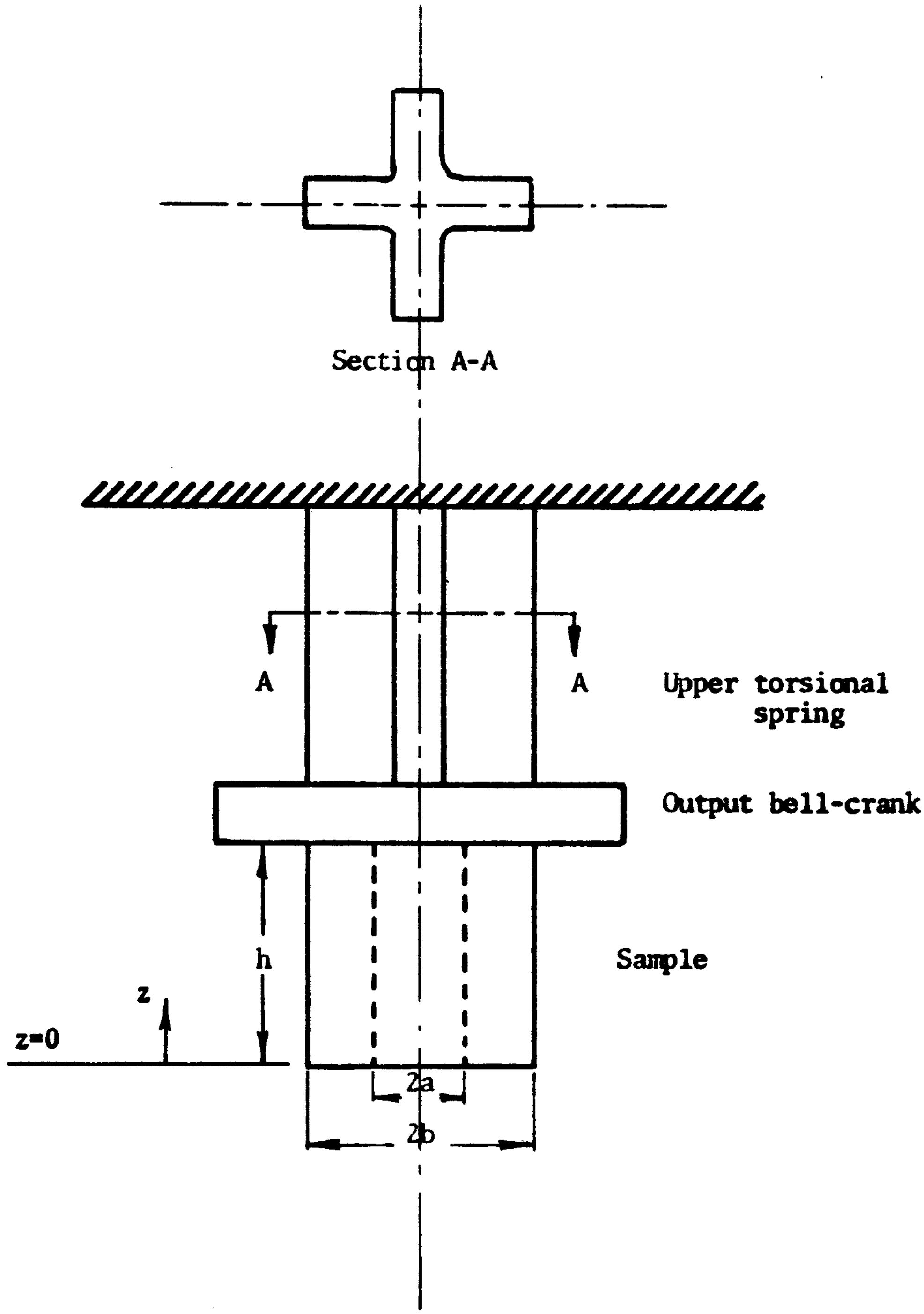


Fig. 7 Sample-Output Bell-Crank-Upper Torsional Spring System

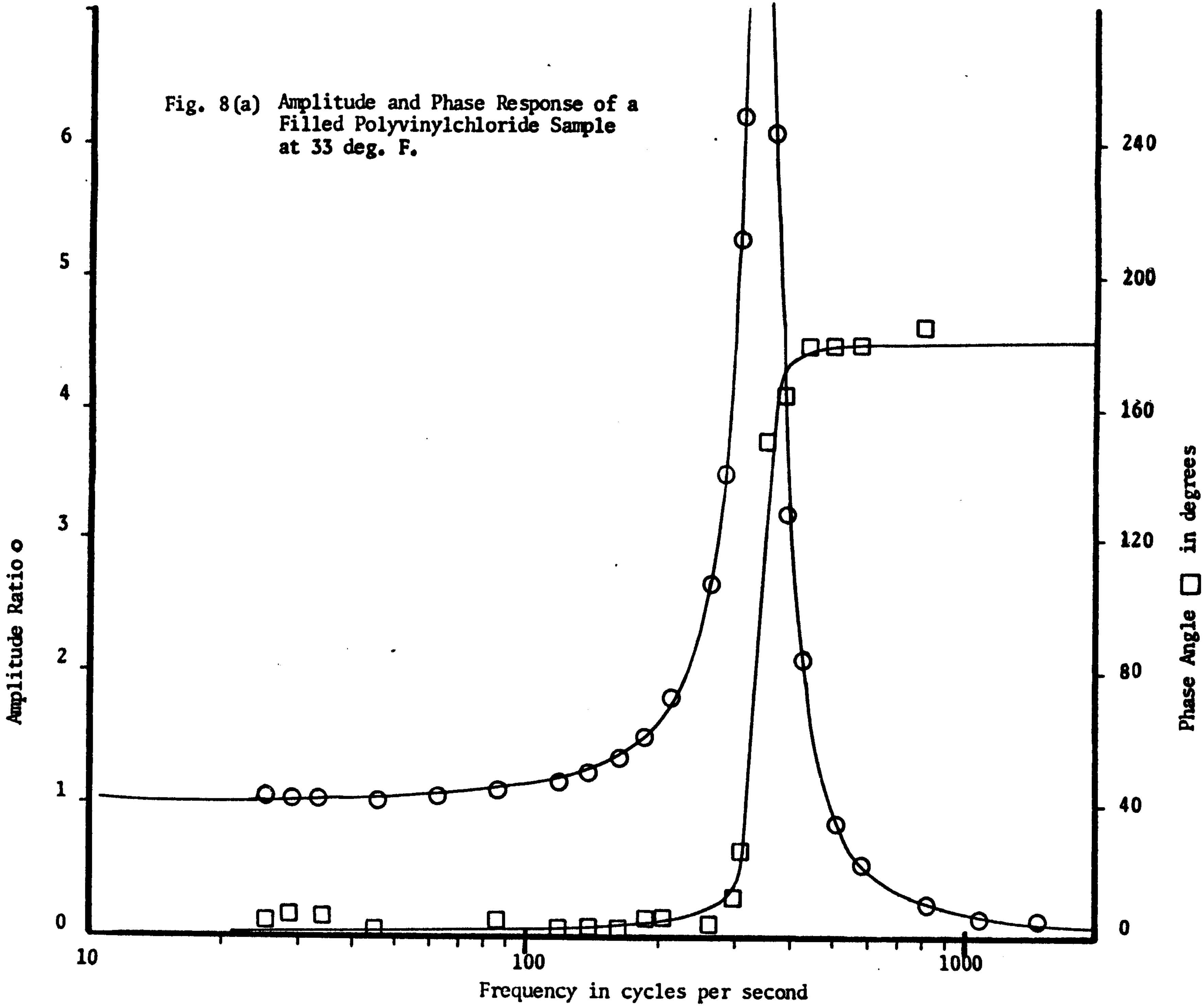


Fig. 8(a) Amplitude and Phase Response of a Filled Polyvinylchloride Sample at 33 deg. F.

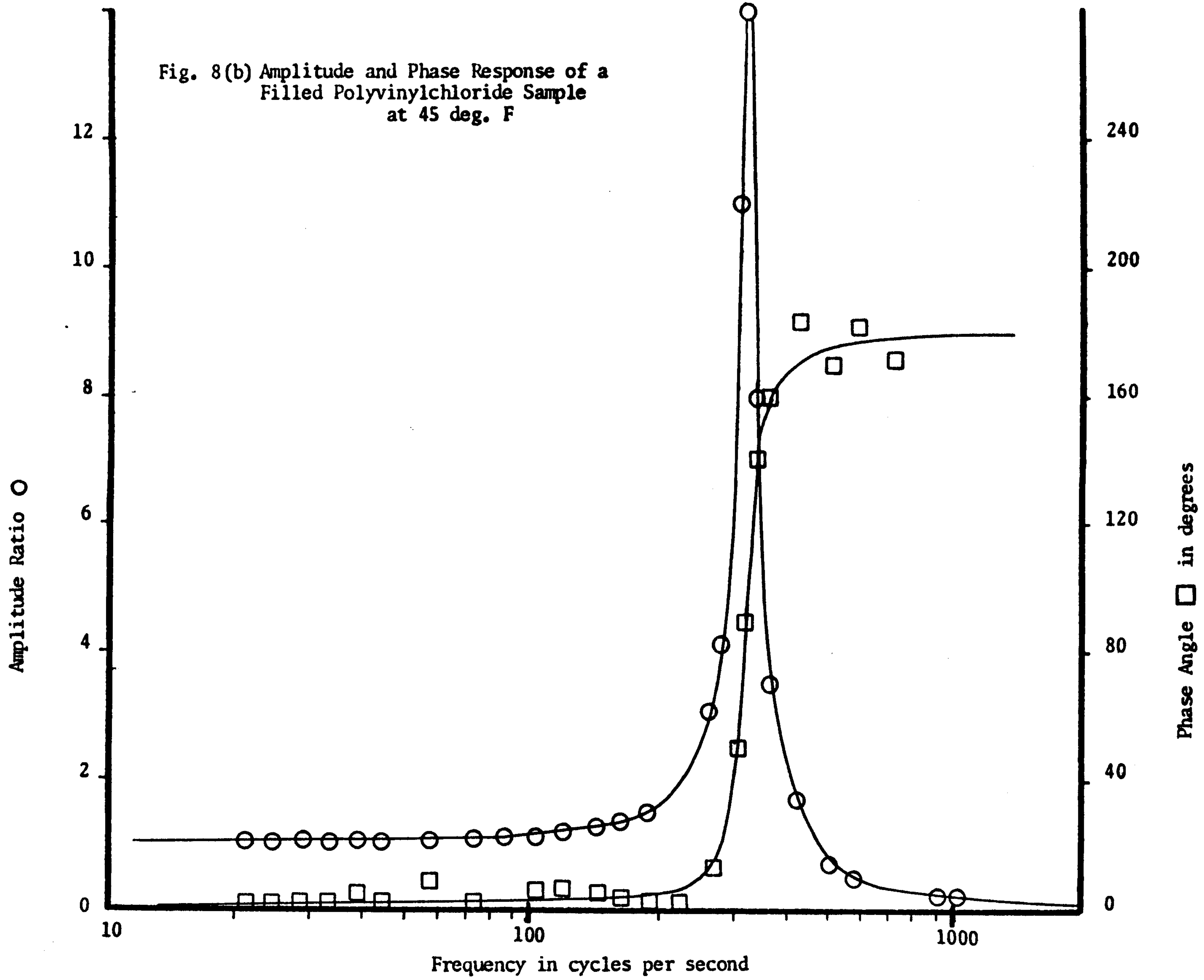


Fig. 8(b) Amplitude and Phase Response of a Filled Polyvinylchloride Sample at 45 deg. F

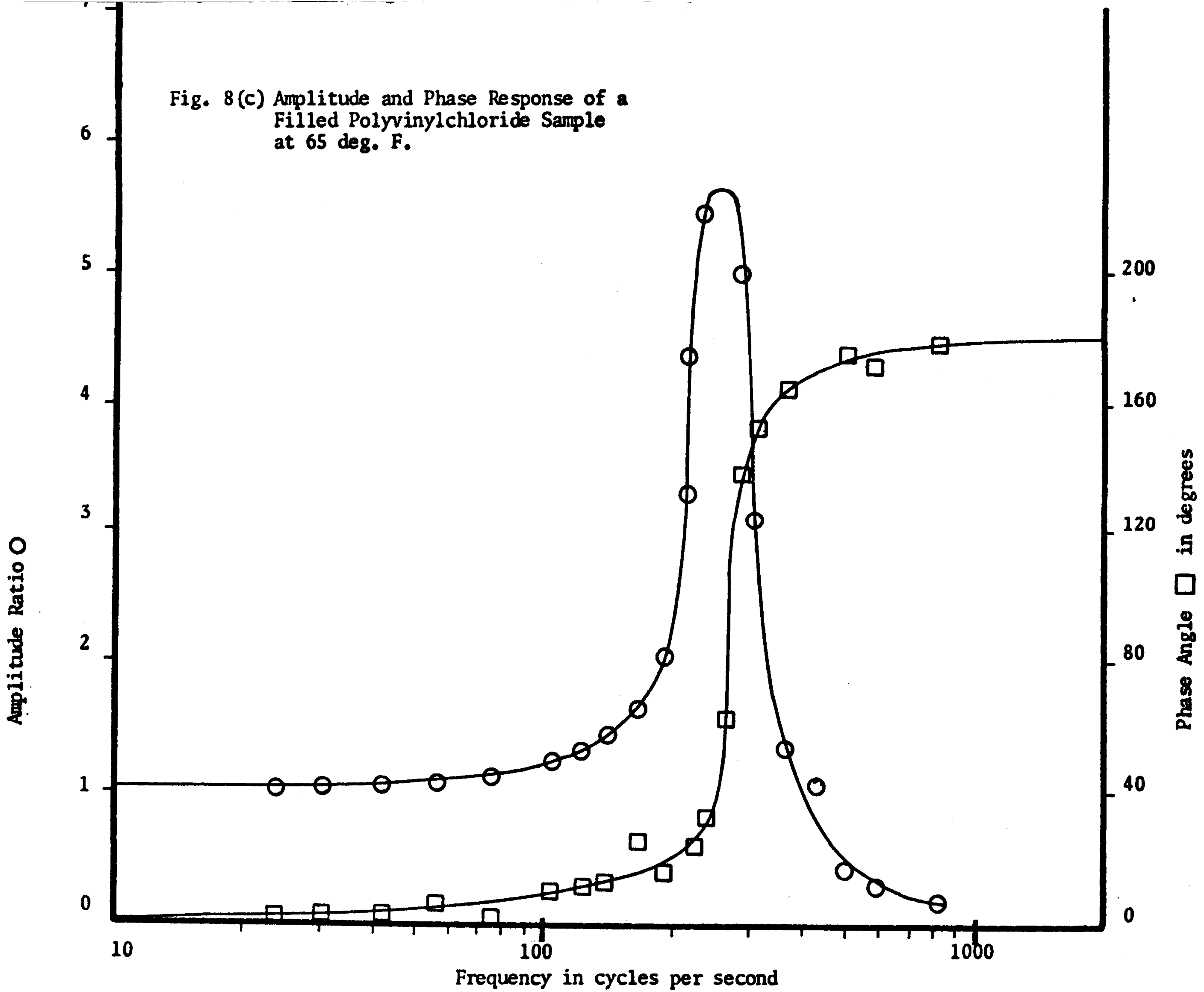
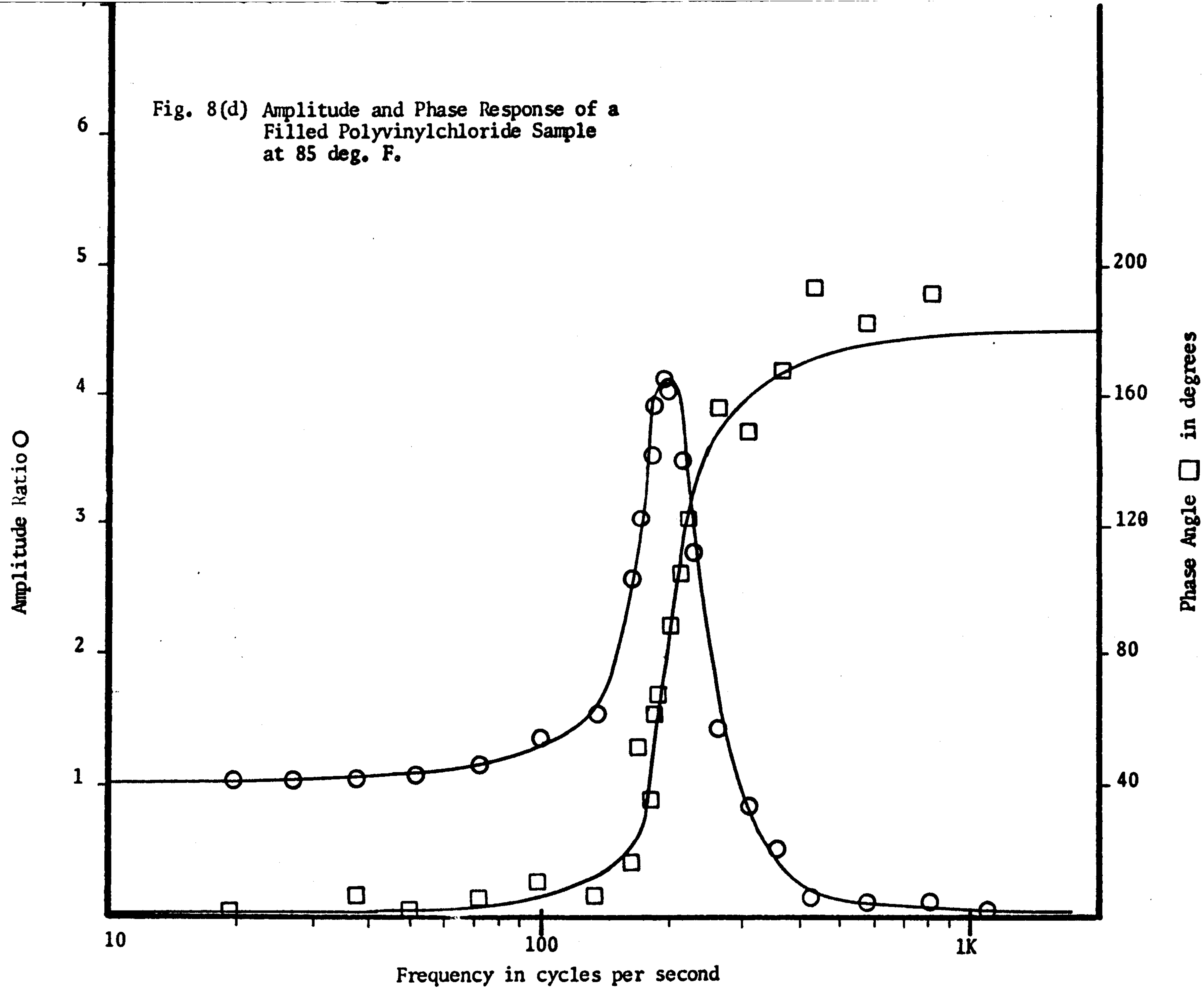


Fig. 8(c) Amplitude and Phase Response of a Filled Polyvinylchloride Sample at 65 deg. F.

Fig. 8(d) Amplitude and Phase Response of a Filled Polyvinylchloride Sample at 85 deg. F.



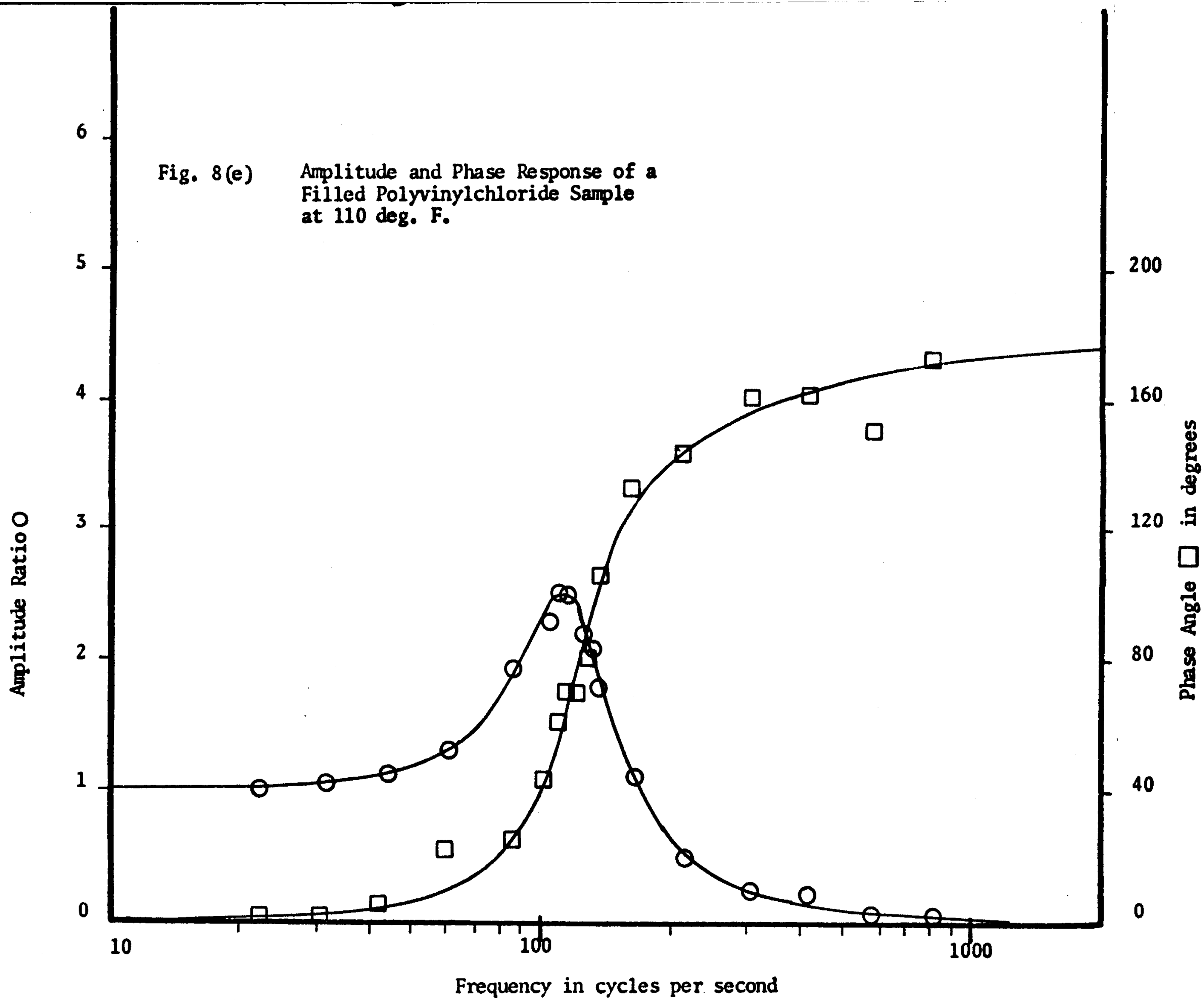


Fig. 8(e) Amplitude and Phase Response of a Filled Polyvinylchloride Sample at 110 deg. F.

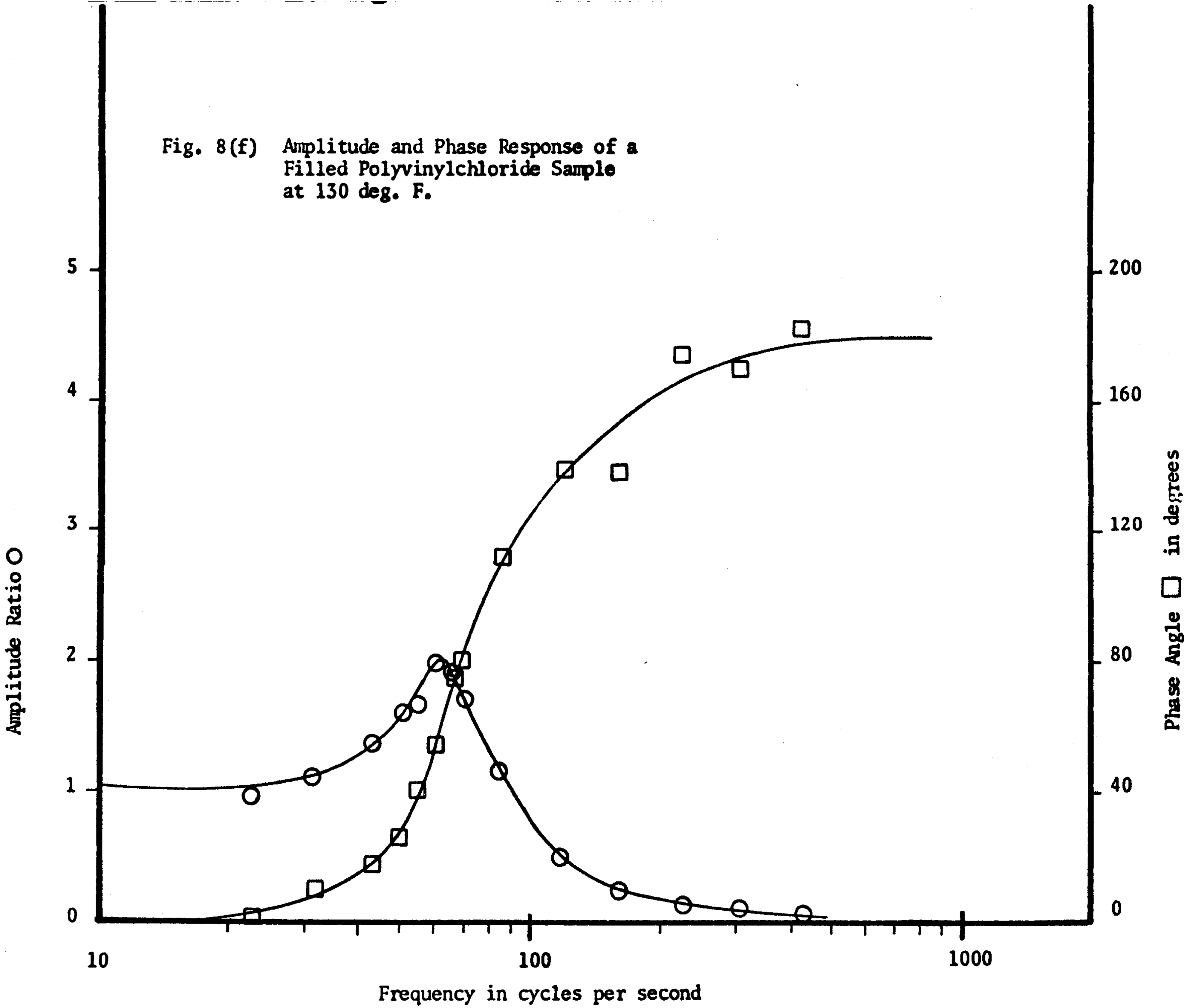


Fig. 8(f) Amplitude and Phase Response of a Filled Polyvinylchloride Sample at 130 deg. F.

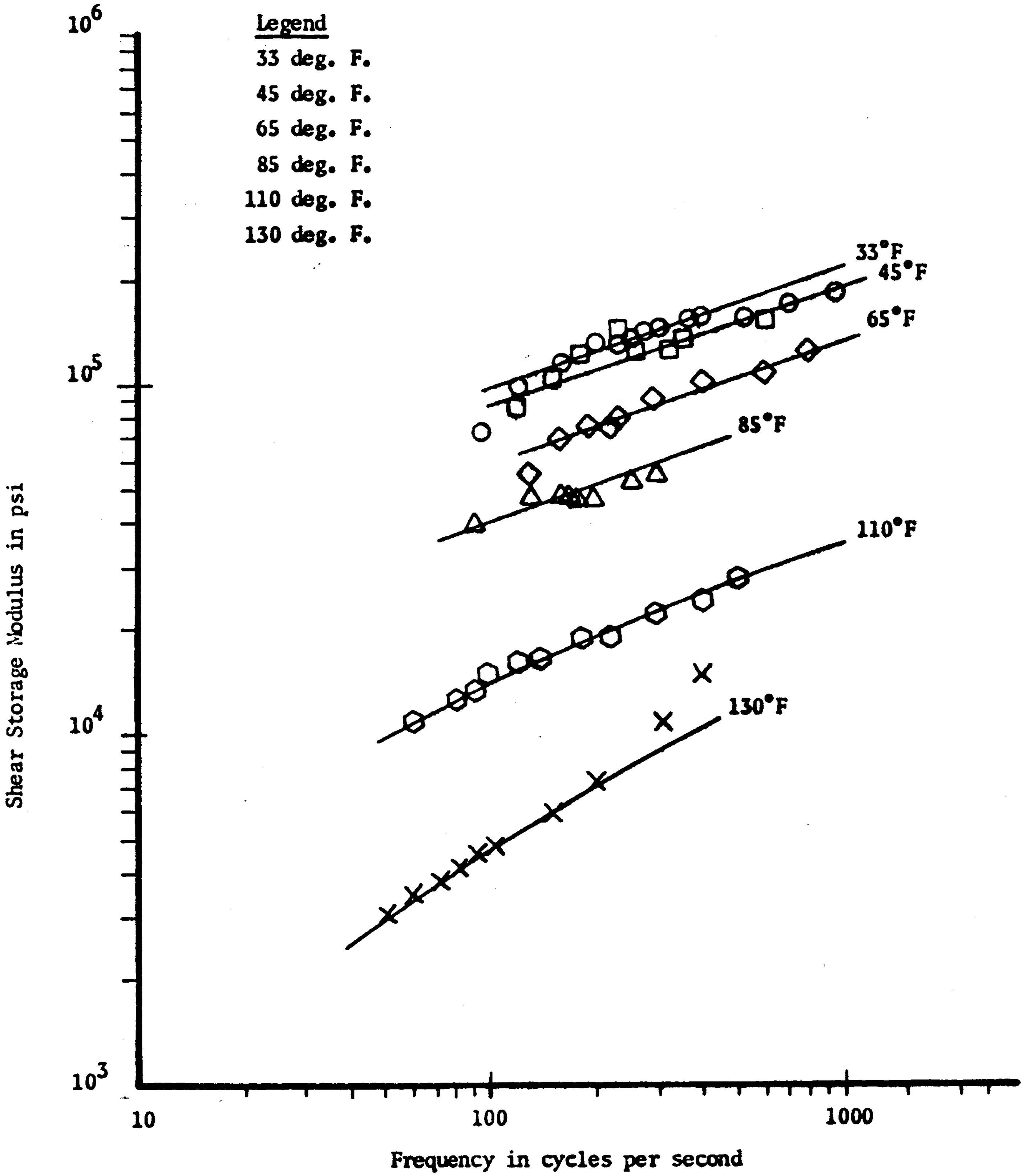


Fig. 9 Shear Storage Modulus versus Frequency for a Sample of Filled Polyvinylchloride

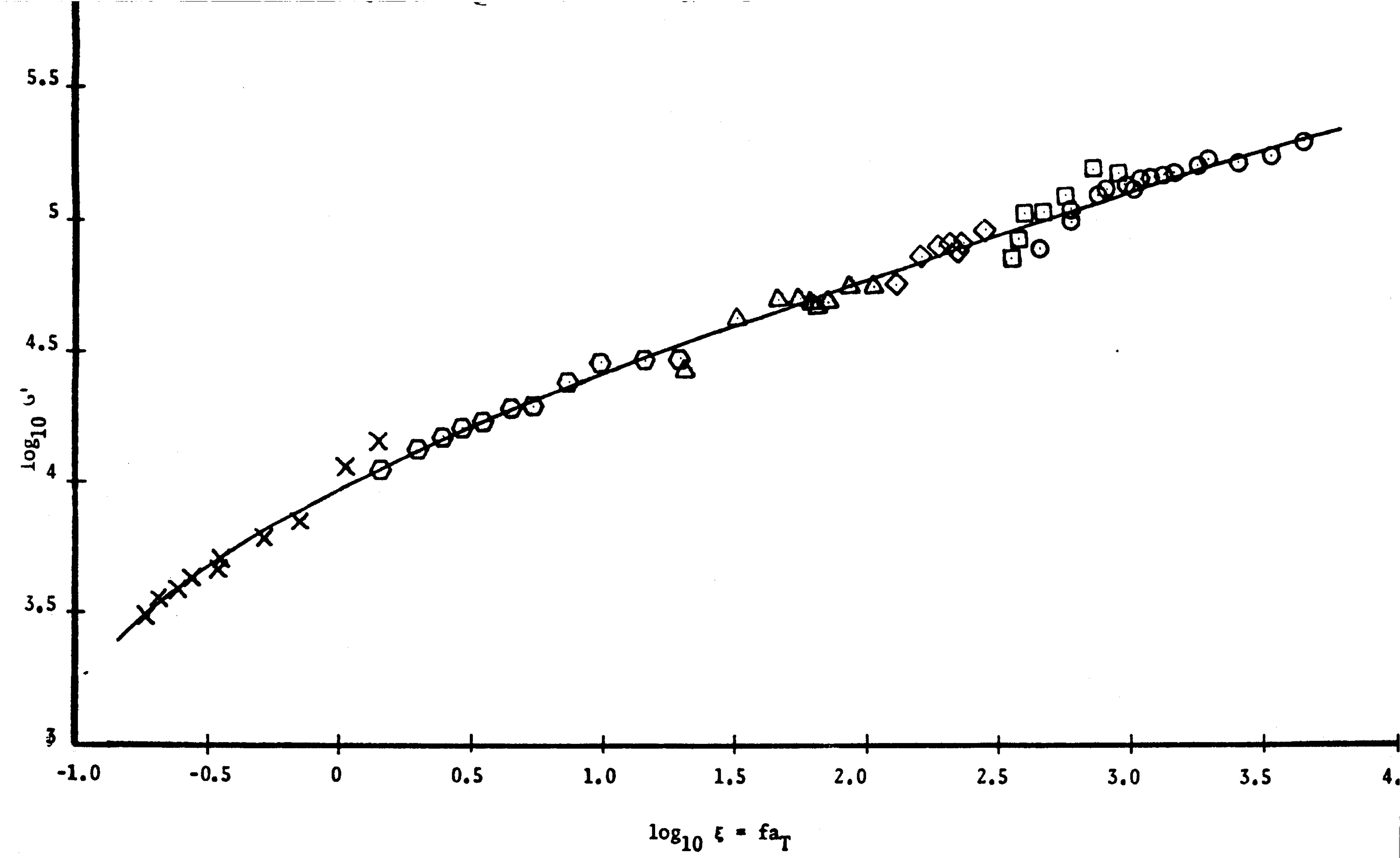


Fig. 10(a) Master Curve for Shear Storage Modulus of a Sample of Filled Polyvinylchloride at 65 deg. F.

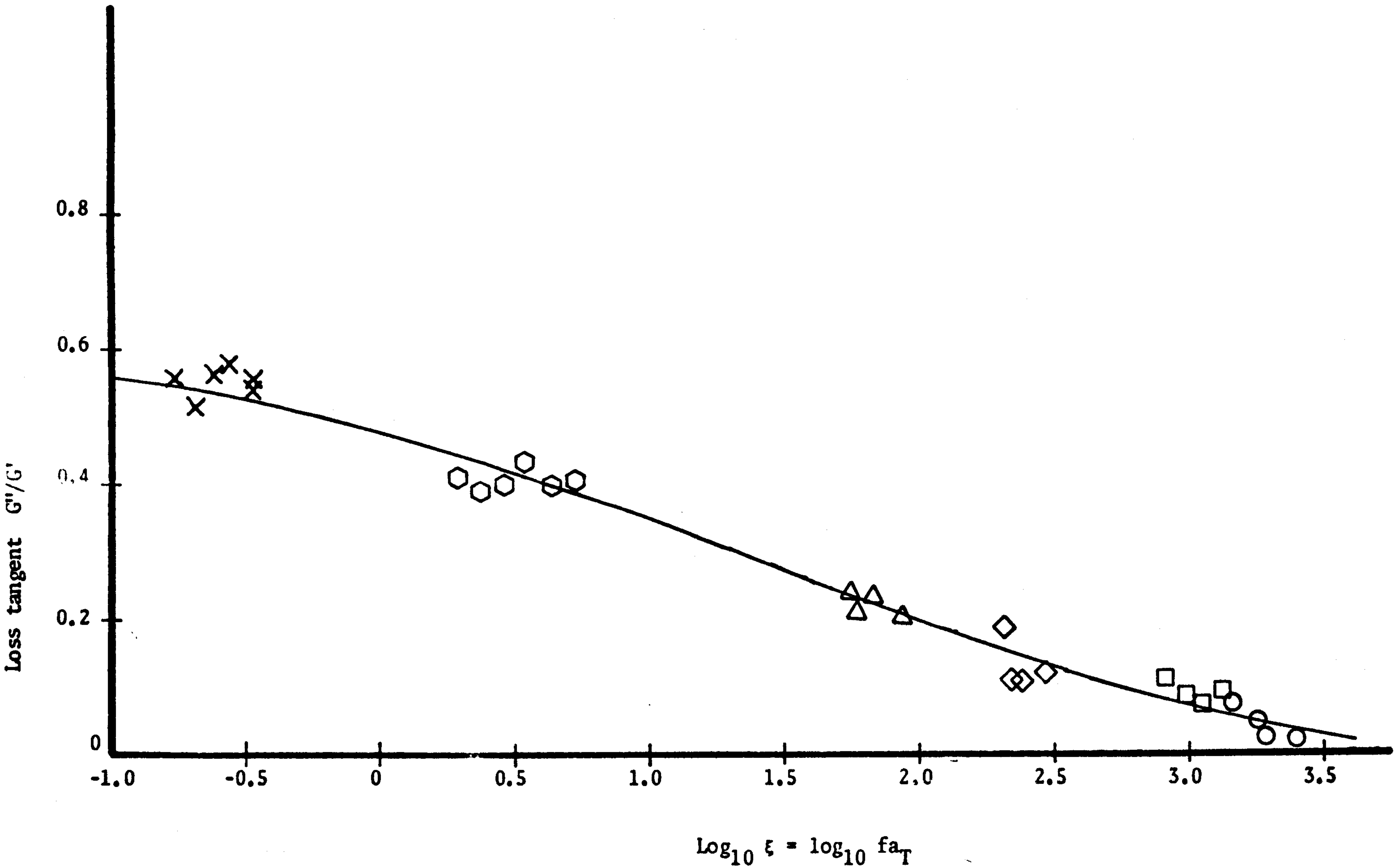


Fig. 10(b) Master Curve for Shear Loss Tangent of a Sample of a Filled Polyvinylchloride at 65 deg. F.

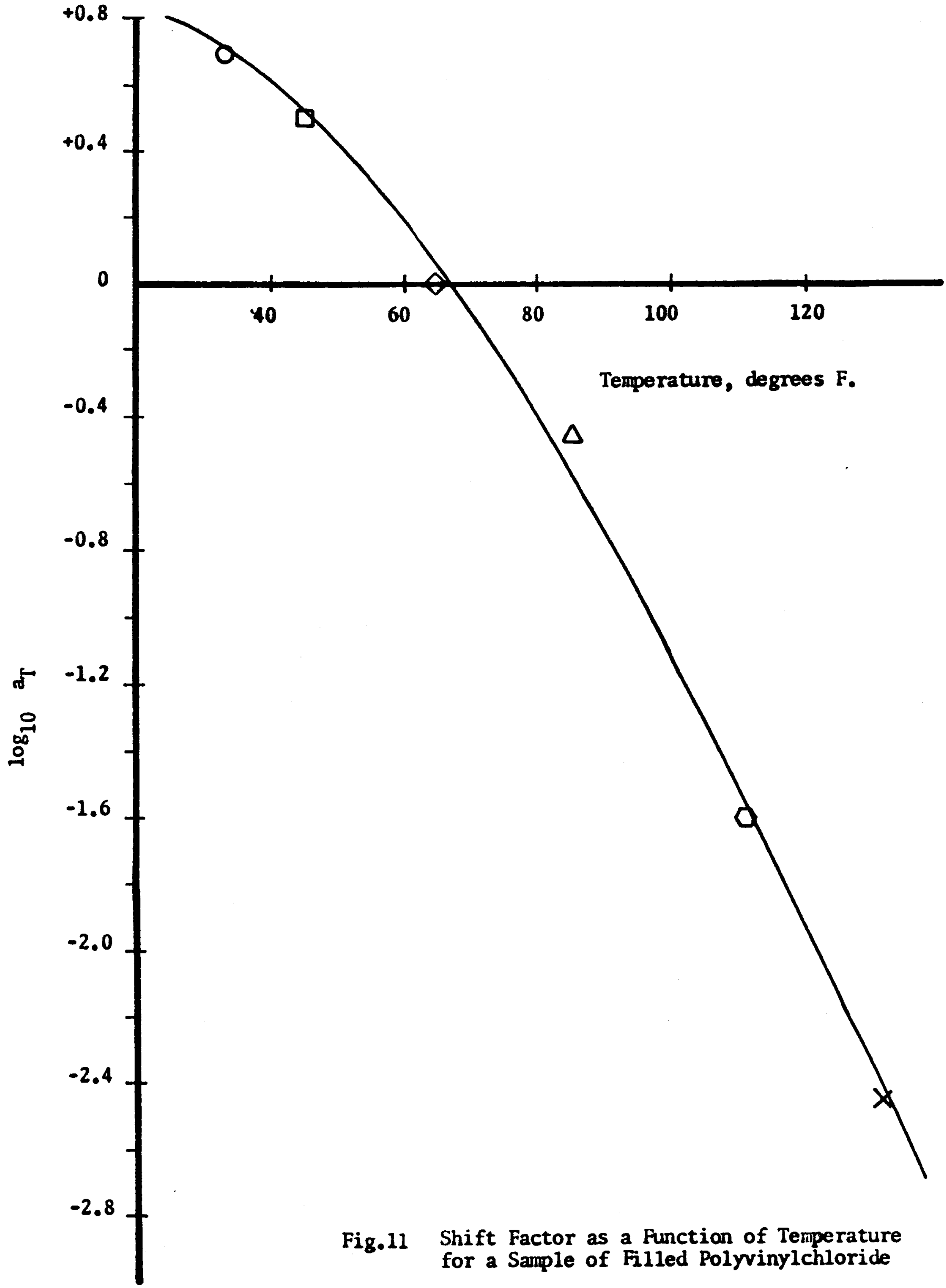


Fig.11 Shift Factor as a Function of Temperature for a Sample of Filled Polyvinylchloride

List of Equipment

Automatic Exciter Control MB 1029 MB Electronics

Power Amplifier MI-200AB McIntosh Laboratory Inc.

Dual Beam Oscilloscope Type 551 with Type CA Preamp
Tektronix Inc.

Dyna-Monitor 2704 Endevco Corp.

True Root Mean Square Voltmeter 320 Ballantine Laboratories, Inc.

Universal Eput and Timer 7360 RW Beckman Instruments, Inc.

Vibration Exciter 390A Goodmans Industries Limited

Band -Pass Filters 315AR & 330MR Krohn-Hite Corporation

Accelerometer 2213C Endevco Corporation

Amplifier 2107 Amplifier 2112 B&K Instruments Inc.

X-Y Plotter 135 F.L. Moseley Co.